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TEXTILE RESEARCH JOURNAL

VOL. XVI, No. 6 June, 1946

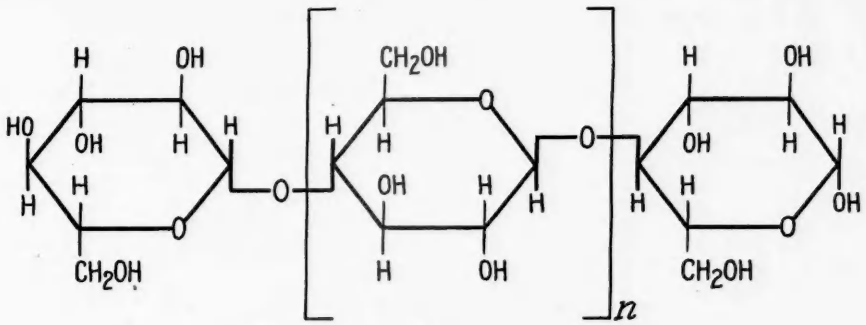
Cellulose Studies

IV. The Chemical Structure of Cellulose and Starch*

Eugene Pacsu and Lejaren Arthur Hiller, Jr.†

Contribution from The Textile Foundation and the Frick Chemical Laboratory at Princeton University

THE present-day generally accepted concept of the chemical structure of the cellulose molecule is the outcome of more than one hundred years of research work. Evidence in favor of a linear macromolecule containing up to 3,000 or 3,500 β-*D*-glucopyranose residues united by 1,4-glycosidic linkages (I) is presented and discussed in recent books, reviews, and monographs on cellulose.



(I)

Likewise, some one hundred and thirty years of research on the chemical structure of starch resulted in the prevailing concept, according to which starch contains at least two constituents which can be separated: amylose and amylopectin, both polymers of α-*D*-glucopyranose, but differing markedly in properties and structure. The minor component, 20 to 30 percent, is represented by an essentially linear arrangement of some 100 to 700 α-*D*-glucopyranose units linked in 1,4-positions (II).

This fraction can be precipitated by addition of higher alcohols, such an *n*-amyl alcohol, or of other polar reagents, such as nitrobenzene. It yields an intense blue coloration with iodine and precipitates rapidly from cold aqueous solution ("retrogradation").

The constitution of the second component, amylopectin, is generally believed to be distinctly different from that of amylose; the giant branched molecules consist of 500 to 2,000 α-*D*-glucopyranose residues

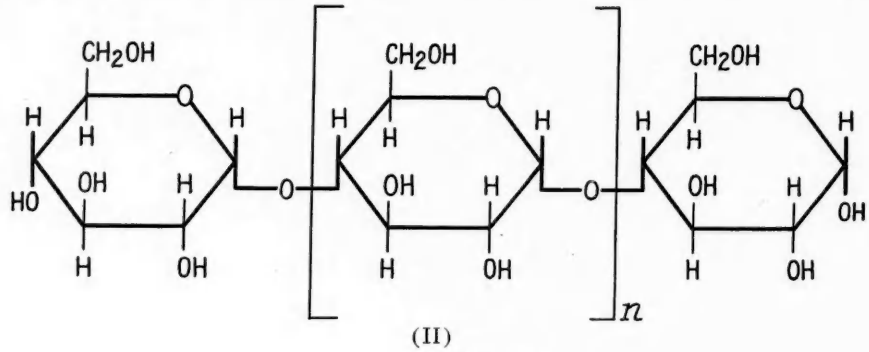
* Manuscript received for publication April 23, 1946. This is the fourth paper in a series—"Cellulose Studies." The first three appeared in the October, 1945, and the March and April, 1946, issues.

† Fellow of the Textile Research Institute.

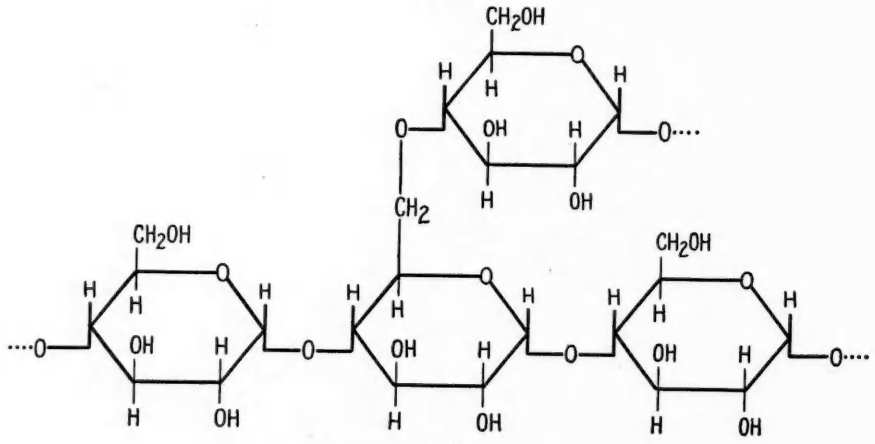
in which, besides the 1,4-glycosidic linkages, branching through 1,6-α-glycosidic linkages occur on the average at every twenty-fifth glucose unit. A branch point of the resulting highly ramified structure is represented by formula (III).

This fraction will not precipitate with the added *n*-amyl alcohol or other polar reagents. It gives a reddish color with iodine and it represents the paste-forming component of starch.

Besides the 1,4-β-glycosidic linkages in cellulose and the 1,4- and 1,6-α-glycosidic linkages in starch, the presence of hydrogen bonds, O—H...O, in both substances is also generally accepted. Such hydrogen bonds are thought to be operative between practically all the hydroxyl groups of neighboring chain molecules, thus holding these individual chains together in a lateral direction.



(II)



(III)

From the results of our recent experiments on cellulose and starch as well as from a critical evaluation of existing data in the literature we have arrived at the conclusion that the present-day concept of both cellulose and starch as embodied in the above structural formulas is inadequate to account satisfactorily for the chemical and physical behavior of these high polymers. In a forthcoming series of articles we shall present and discuss in detail evidence in favor of a new concept concerning the composition and structure of cellulose and starch. In the present preliminary publication only a broad outline will be given—a summary of the final conclusions we have drawn from the results of our experiments and from new interpretation of existing data.

General Outline of the Proposed Structure of Cellulose and Starch

The main feature of our concept is based on the recognition of the fundamentally important role played by minute quantities of small molecules, such as glucose, cellobiose, cellotriose, etc., and glucose, maltose, probably maltotriose, etc., which are incorporated, respectively, in the cellulose and starch molecules. These simple sugars occur in their hydrated open-chain forms and hold the long-chain molecules together by means of semiacetal linkages between the hydrated aldehyde groups and any of the alcoholic groups of the glucose units in the main chains. They are regarded as chemical flaws in the fibers or in the starch granules because of the great sensitivity of

their semiacetal linkages toward oxonium ions, H_3O^+, which catalyze the hydrolytic scission of such bonds entirely out of order of the regular glycosidic bonds. Once these strategically most important simple sugars are removed from the fiber by mild treatment with acid, the cellulose loses completely its tensile strength and becomes "hydrocellulose," a brittle, powdery material. Further treatment of this material by somewhat stronger acid does not cause any appreciable change in its physical or chemical properties. Since the semiacetal linkages are very stable toward OH'-ions, treatment of cellulose by dilute alkali does not produce a similar effect.

In the case of starch a very small concentration of H_3O^+-ions is sufficient to cause the complete destruction of the elaborate network of molecular chains which are built up by frequent "branching" through semiacetal linkages of the glucose, maltose and probably maltotriose, maltotetrose, etc., molecules. Indeed, in the usual practice of autoclaving the gelatinized starch for several hours at 18 to 20 pounds pressure and at pH 5.9 to 6.3 there are enough oxonium ions present to catalyze the hydrolytic scission of a considerable portion of the semiacetal linkages, with the production of the "amylose component." As to the "amylopectin component," which in reality represents an unattacked portion of the original starch structure, this can be easily converted by similar acid treatment into the "amylose component."

In the following paragraphs a brief résumé of our forthcoming publications is given.

Cellulose

1. Determination of the Terminal Reducing Groups

We have found that an excess of $0.1N$ potassium permanganate solution in the presence of dilute sulfuric acid at 0°C selectively oxidizes the terminal (semiacetal) groups of the open-chain glucose units in cellulosic materials. The ortho-acid forms, $-C(OH)_2OR$, of the gluconic, cellobionic, etc., acids thus produced remain incorporated in the fibers. From the amount of potassium permanganate consumed the reducing-group contents of the various samples can be determined. The values are reproducible and, since the reagent appears to be quite selective under the experimental conditions, in our opinion they are more reliable than those obtained by the use of alkaline hypoiodite, which is known to cause overoxidation.

2. Determination of Carboxylic Groups

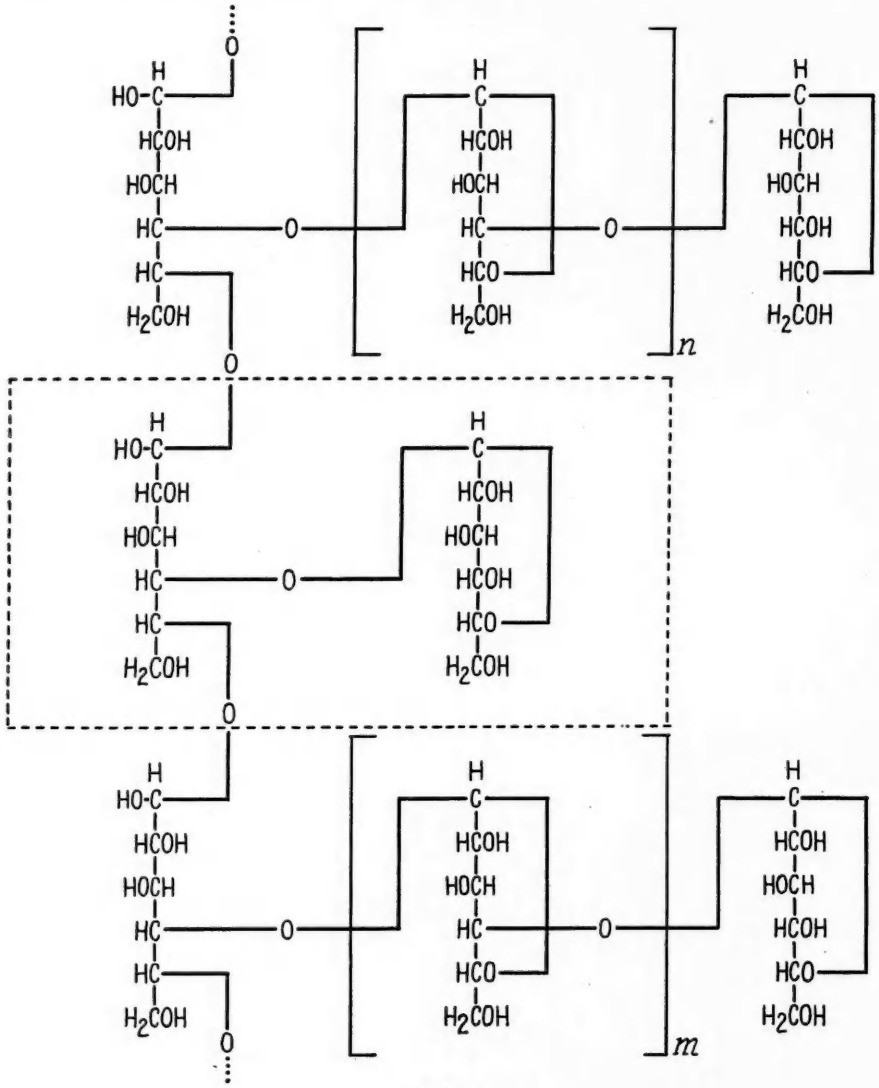
Carboxylic groups can be quantitatively estimated by addition to the well-prepared cellulosic materials, which are suspended in distilled water, of a slight excess of $0.02N$ alkali and titration of the excess alkali with $0.02N$ hydrochloric acid to a sharp endpoint in the presence of phenolphthalein, or to a certain pH value electrometrically. The method gives excellent results and the values obtained can be easily reproduced. We used this procedure to check the results obtained previously in the estimation for the reducing groups by the potassium permanganate method; the alkali consumption was nearly one-half the amount of the potassium permanganate used for the oxidation as required by the stoichiometric equation: $-CHO + O \rightarrow -COOH$.

3. The Nature of "Hydrocellulose"

It was most surprising to find that after comparatively mild acid treatment, such as keeping cellulose in $2N$ sulfuric acid at 60°C for 6 hours, the resulting powdery "hydrocellulose" contained *fewer* reducing end-groups than the original material did. The lost material, a very minute amount, was found in the acid solution and it was determined quantitatively as glucose. Subsequent treatment of this "hydrocellulose" with somewhat stronger acid caused a further, but much smaller, drop in the reducing-group content of the sample. Hydrolysis of true β-glycosidic linkages would, of course, create new aldehyde groups, which would cause a rise in the reducing-group content of the material. Such a rise in the values of the reducing groups is, indeed, reported in the literature. But the estimations were carried out by employment of alkaline hypoiodite solutions which are known to give unsatisfactory results. In order to clarify this important point, we have dissolved cellulose in 65-percent sulfuric acid and determined the reducing groups after an interval of 60 minutes; the aldehyde content was only a little higher than in the "hydrocellulose" obtained by the mild treatment with dilute acid. Clearly, the initial rapid effect of dilute acid on cellulose, the drop in the reducing-group values, and the appearance of glucose or cellobiose in the acid filtrate indicate that during this important phase of hydrolysis other than normal glycosidic bonds are broken. We believe that these bonds are semiacetal linkages and probably a few acetal linkages.

4. Viscosity of Cellulose in Phosphoric Acid

It is known that cellulose readily dissolves in 85-percent phosphoric acid to give rise to a very viscous solution. However, the viscosity of this solution suffers a tremendous drop during a period of 24 hours. Whereas the molecular weight calculated from the initial viscosity of our sample gave a value of more than 100,000, the molecular weight derived from the viscosity of the aged solution was only a few hundred. The reducing-group content of the material in the aged solution, on the other hand, was almost identical with that found in the 65-percent sulfuric acid solution or in the powdery "hydrocellulose" sample, giving a molecular weight of several ten-thousands. Obviously, the cause of this inordinate change in viscosity cannot be ascribed to hydrolysis of true glycosidic bonds. This conclusion is confirmed by the fact that the optical rotation of the freshly prepared viscous solution remains constant at about $[\alpha]_D^{20} = 0°$, not only during the period of change in viscosity but also during an observation period of several weeks. Glucose, on the other hand, under comparable conditions, shows an initial specific rotation of $+68°$, which value remained constant during an observation period of several days. These facts led us to the conclusion that gradual hydrolysis of semiacetal linkages and not of true glycosidic bonds is responsible for the striking change in the viscosity of cellulose in phosphoric acid.

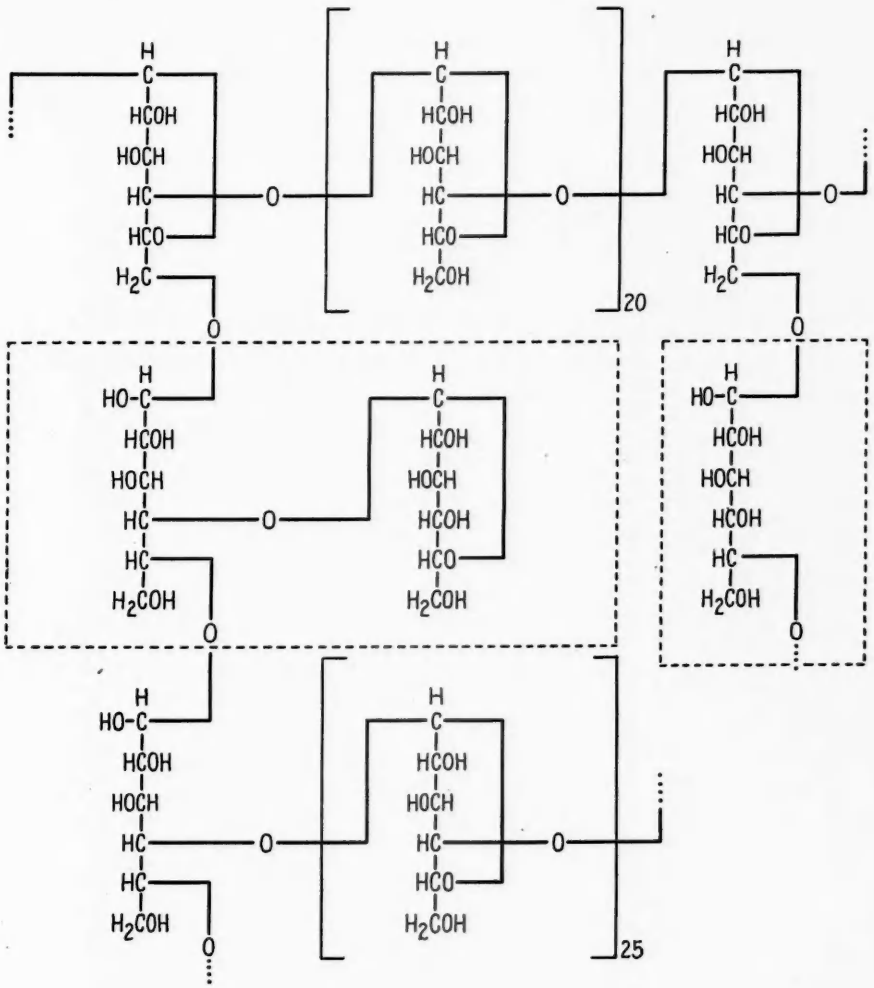


(IV)

5. *The Structural Formula of Cellulose*

On the basis of the foregoing findings we propose a new formula for cellulose (IV), in which long molecular chains are held together by the semiacetal linkages of glucose, cellobiose, cellotriose, etc.

The "branching" may occur at any glucose unit at the main chain and at any of the OH-groups of such



(V)

unit. Taking into account the results of the methylation experiments, we believe that formula (IV) adequately represents the chemical structure of a portion of a cellulose molecule, in which two molecular chains are held together by a cellobiose molecule. Occasional occurrence in the fiber of true acetal linkages originating from glucose, cellobiose, etc., molecules is not only possible but it is probable.

Starch

1. *The "Fractionation" of Starch*

The yield of the "amylose component" of starch appears to be a function of the concentration of the H_3O^+-ions. We have found that both inorganic acids, such as 0.1*N* sulfuric acid, and organic acids, such as formic, citric, and even acetic acid, supply oxonium ions in sufficient concentration to hydrolyze almost completely at 86°C the semiacetal (possibly also acetal) linkages in starch to give rise to a material which shows the characteristic properties of the "amylose component" (retrogradation, precipitation with polar reagents, blue coloration with iodine). The "amylopectin component," usually ob-

tained by the pentasol separation method, yields red coloration with iodine either because it consists of inherently short chains or because it represents an unattacked portion of the original starch structure, where frequent "branching" through semiacetal linkages in the long, helical chains leaves too-short chain intervals to accommodate the iodine molecules in the interior of the helices. In the latter case, mild hydrolysis by H_3O^+-ions will "liberate" the long chains, with the production of a new portion of the "amylose component." Commercial waxy maize starch, which consists mainly of inherently short chains, gives rise to a small quantity of "amylose component" on treatment with 0.1*N* sulfuric acid at 86°C.

Of the two enzymes, α- and β-amylase, the former acts as a "semiacetalase"; it splits starch first (liquefaction) by hydrolyzing most of the semiacetal linkages, with the production of "dextrin," maltose, and glucose. The latter most likely represents the original glucose molecules which hold the long chains together by semiacetal linkages. The "dextrin" may contain "branched" portions of chains, where the semiacetal linkages occur at OH-groups other than at position 6, thus rendering the dextrin unsuitable for the enzyme as a substrate. β-Amylase rapidly attacks the long-chain portion of the starch molecule without liquefaction. The products are maltose and some 45 percent of a high molecular-weight breakdown product (residual-dextrin I). The latter still contains the original semiacetal linkages originating from glucose, maltose, maltotriose, etc., molecules and is, therefore, hydrolyzed at those points by α-amylase, α-glucosidase and even by superheated water (H_3O^+-ions). By this reaction further long-chain molecules are exposed for the attack of the β-amylase, to give rise to maltose and a residue which consists of chains too short to be attacked by β-amylase.

2. The Structural Formula of Starch

On the basis of the foregoing findings we believe that there are not two or more components in starch. The granules themselves represent a visible "molecule" which is a three-dimensional network of shorter and longer chains held together on the average at every twentieth or twenty-fifth glucose unit through the semiacetal linkages of mostly glucose, but also of maltose, maltotriose, etc., molecules. The semiacetal linkages may involve any of the OH-groups of the chain units in harmony with the results of methylation data. Minute quantities of orthophosphoric acid may also take part in cross-linking individual chains through two ester linkages. A portion of the starch network is represented by formula (V).

In conclusion we should like to point out that this new concept of cellulose and starch structure, in our opinion, eliminates many of the present difficulties concerning the interpretation of existing experimental facts. It also opens up new possibilities in both fundamental and industrial research, and clearly shows the road for improvement by employment of H_3O^+-pretreated starch and cellulosic materials in certain industrial processes, as in the manufacture of esters, ethers, and xanthates of cellulose and starch, in the modification of starch by enzymes, and in the paper and textile industry in general. It is very probable that, in the details, our structural formulas will need some modifications, which, we hope, will come through the critical approach of other workers in these fields.

The Outer Wall of the Cotton Fiber and Its Influence on Fiber Properties

Thomas Kerr*

MANY properties of cotton fibers are influenced by the outer covering, which is known to be different from the inner wall. Rollins [12] has recently emphasized the conception that there are two outer layers in the cotton hair. It is the purpose of this paper to discuss the structure of these outer layers and to show their relation to fiber morphology.

Previous Work

Before considering cotton, it seems advisable to consider the structure of wood cells in order to show that there is a fundamental pattern of layering in plant fibers. According to Kerr and Bailey [10], the following components are commonly present in wood and bast fibers: (1) primary wall and (2) secondary wall consisting of (*a*) an outer layer, (*b*) a central layer, and (*c*) an inner layer. The thin primary wall (less than a micron in thickness) is the membrane of the fiber during the period of cell enlargement. It can be distinguished from the secondary thickening by its staining, lack of intense birefringence, and the fact that it is the only layer completely covering the cell in the region of the pit areas. After the fibers have reached their mature dimensions, a secondary wall is deposited beneath the primary membrane. This wall thickening is differentiated into three regions on the basis of cellulose orientation. In the narrow outer and inner layers (each approximately one micron in width), the cellulose fibrils make an angle of more than 45° with the long axis of the fiber. The central layer, varying in thickness in different cells, commonly consists of cellulose chains oriented parallel or making a small angle with the long axis of the fiber. The outer and central layers of the secondary wall are present in practically all types of wood fibers, but the inner layer may be absent.

In cotton hairs, primary and secondary walls are easily differentiated [1, 9]. The primary membrane, less than a micron in width, stains heavily with basic dyes, while no visible staining can be detected in the secondary thickening. The slightly birefringent primary wall contains cellulose apparently oriented in a net-like structure with its major extinction position, as viewed between crossed nicols, at right angles to the fiber axis. The orientation of the cellulose in the primary wall can be seen, however, only by staining young fibers with substantive dyes, such as Congo red, and then viewing between crossed nicols. In a previous paper [1], a single primary wall was considered to possess two helices (one *S* and *Z* spiral) the fibrils of each helix oriented at approximately 65° to 70° to the fiber axis. A third orientation at right angles to the main fiber axis was also indicated. Frey-Wyssling [6] has pointed out that the pattern of the primary wall seen between crossed nicols could be caused by a single layer having a structure somewhat similar to that of a stretched tennis net. The primary wall is the only covering enclosing the protoplasm of the cotton hair during the period of cell elongation —that is, during the first 15 to 18 days of development. After

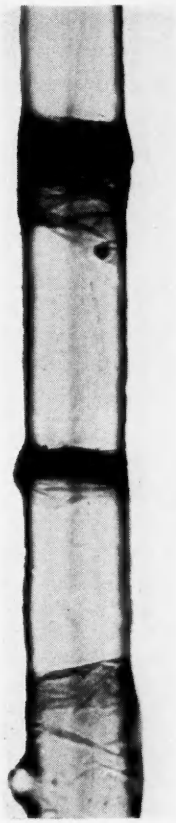


FIG. 1. *Mature but undried cotton fiber scraped with dull knife. Primary wall stained with Ruthenium red, thrown into folds exposing unstained secondary wall. Magnification 550 ×.*

* Cytologist, Division of Cotton and Other Fiber Crops and Diseases, Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture and North Carolina Agricultural Experiment Station. Published with the approval of the Director of the North Carolina Agricultural Experiment Station as Paper No. 237 of the Journal Series.

the hairs have reached their full length a secondary wall is deposited on the inner surface of the primary membrane and wall thickening continues for two or three weeks at the expense of the cell lumen. The secondary wall consists of strongly birefringent cellulose oriented in a helix at an angle of 25° to 45° to the main fiber axis. The direction of the helix changes many times from an *S* to *Z* spiral * along the length of the hairs, and each place that the direction of the helix changes is known as a reversal.

In studying the structure of the cotton hair, differentiation of the secondary wall into two or three layers on the basis of cellulose orientation, similar to that found in wood fibers, did not seem to be possible [1]. All parts of the secondary wall show a pronounced spiral structure, and for this reason layering cannot be distinguished in cross sections by variations in birefringence. However, Hock, Ramsay, and Harris [9] found that when depectinized fibers are swollen in cuprammonium hydroxide, a thin outer layer is present which possesses a helical structure with reversals along the length of the hair. Where this outer layer has an *S* spiral, the main part of the wall possesses a *Z* spiral and vice versa. Hock, Ramsay, and Harris [9] identified this outer layer as the outermost part of the secondary wall and called it the "winding." Anderson and Kerr [1] had previously presented evidence that the outermost layer of the secondary wall may be distinguished at times from the succeeding layers during cell wall development.

The Winding

On the basis of orientation, the winding would be homologous to the outer layer of the secondary thickening in wood fibers. However, Hock, Ramsay, and Harris [9] identified this layer after the removal of the waxes and pectic substances, and then only by swelling the purified fibers. The question arises as to what has happened to the cellulose of the primary membrane since this treatment would not dissolve it. Hock and Mark [8] state that the primary wall is removed following the treatment recommended by Worner and Mease [13]. When primary walls from developing material are treated in this manner a skeleton of cellulose persists. It has been suggested that the so-called winding represents solely the cellulose of the primary wall reoriented by the anisotropic swelling of the secondary thickening. Critical evidence on this point was obtained by mechanically removing the primary wall from undried but mature fibers—that is, from cotton taken from a boll that had cracked but had never been allowed to dry. These fibers were first stained with Ruthenium red, then combed and scraped lightly with a dull knife. In many places along the length of the hairs, the heavily stained surface covering (the primary wall) was ruptured and thrown back into folds, exposing an unstained wall beneath (Figure 1). When this material was slightly swollen in cuprammonium hydroxide (Figures 2 and 5), the places from which the primary membrane had been removed usually showed another outer layer that could be identified as the winding—a layer possessing

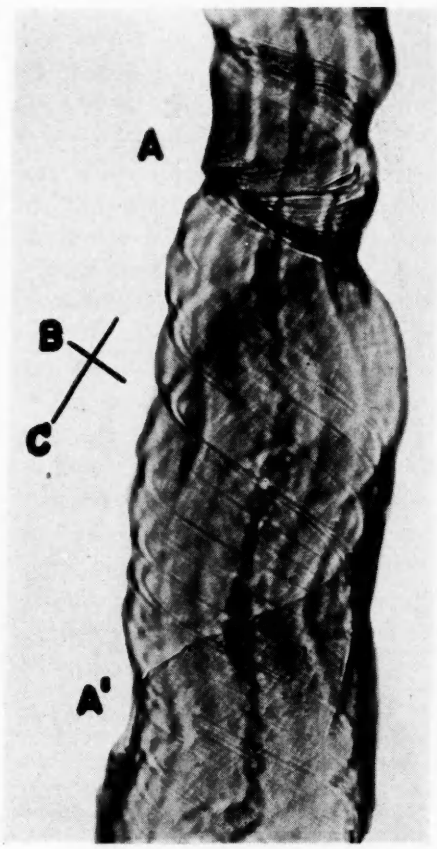


FIG. 2. *Mature but undried cotton fiber swollen in cuprammonia. Primary wall stained with Ruthenium red remains at A and A'. Direction of cellulose orientation in winding (B) and wall-thickening (C) indicated. Magnification 750 ×.*

* Hock, Ramsay, and Harris [9] refer to *S* and *Z* twists, adopting their terminology from the *A.S.T.M. Standards on Textile Materials* (Philadelphia, 1941) where it has been used to denote the twists of yarns. A yarn has an *S* twist if when it is held in a vertical position the spiral conforms in slope to the central portion of the letter *S*. Conversely, the yarn has a *Z* twist if the spiral follows the form of a letter *Z*. The *S* and *Z* terminology is extremely helpful in describing the spirality of cellulose fibrils but the word "twist" does not seem to be appropriate since the cellulose is deposited in a spiral manner and is not twisted.

an *S* spiral when the main part of the wall had a *Z* spiral.

The winding may be demonstrated by a number of swelling techniques, and Hock, Ramsay, and Harris [9] have concluded that the orientation of the fibrils immediately beneath the outer winding is invariably in the opposite direction. If this is true, it would seem that the points of reversal in the winding and in the other layers of the secondary wall would always occur simultaneously. This cannot be verified from developmental material—that is, with fibers taken from bolls 2 to 5 days after the beginning of secondary deposition and stained with chlorozinc iodide [1]. The points of reversal in the outermost layer of the secondary wall frequently do not coincide with the points of reversal in the second layer of thickening.* As a result of this variation in reversal points, all layers of the secondary wall, including the outermost layer, may spiral in the same direction in certain places along the length of the hair (Figure 3). In mature fibers there are always a number of places where the winding cannot be demonstrated. This may be explained by difficulties in the technique but it may also indicate that all layers of the secondary wall may have essentially the same orientation. From the swelling behavior of dewaxed and depectinized fibers, the winding can be demonstrated in at least 80 percent of the fiber length. However, since the winding is differentiated chiefly by its opposite orientation from the other lamellae of the secondary thickening, it cannot be considered a complete layer in the same sense as the primary membrane can.

The Wall Thickening

The wall thickening (that is, the secondary wall without the winding) may be considered as a unit. It has a homogeneous appearance in cross sections although when swollen in cuprammonium hydroxide the presence of layering, referred to in literature [1, 9] as growth rings, may be demonstrated. In the swollen condition alternate zones stain deeply and lightly with substantive dyes and show a marked difference in birefringence. This type of layering has been considered to be caused by differences in the density or porosity of the cellulose in alternate lamellae [1, 2]. There are no breaks in the radial continuity of the wall and, as far as one can determine, there are no striking differences in the orientation of the cellulose fibrils associated with the growth-ring structure. However, the microscopic determination of the cellulose orientation throughout the thickness of the secondary wall presents considerable difficulties. The direction of the fibrils in successive lamellae cannot be seen without swelling, and when native fibers are treated with cuprammonium hydroxide the restricting action of the outer layers obscures the picture. If this restricting action is destroyed by pretreatment with hot dilute acid, the orientation of the cellulose in successive layers may be seen between crossed nicols in swollen fibers. The inner layers do not expand as much as the outer part of the wall and, correlated with this difference in swelling, there is a gradual increase in birefringence as one focuses through successive lamellae. By studying these preparations, it may be seen that the fibrils do not change from an *S* to a *Z* direction in any one place throughout the wall thickening; they apparently follow the pattern laid down in the second layer of secondary deposition. On the other hand, variations in the steepness of the helix in different growth rings (from 25° to 35°) have been found. This type of variation may be caused by the swelling, since it is known that such treatments alter the angle which the spiral makes with the major axis of the fiber. However, differences in the steepness of the spiral throughout the wall thickening would explain variations in x-ray patterns which have occurred in developmental studies [4].

In most cotton fibers a clearly defined inner or lumen layer cannot be differentiated, although occasionally in dried hairs the innermost part of the wall stains with basic dyes. This staining appears to be caused by the protoplasmic remains and has not been observed in mature hairs that have never been al-

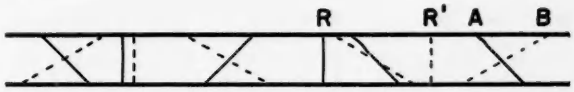


FIG. 3. *Diagram showing relation between the cellulose orientation in the winding, solid line, and in the wall thickening, broken line, as affected by variations in the reversal positions. Solid lines indicate orientation (A) and reversal point (R) of winding. Dotted lines indicate orientation (B) and reversal point (R') of wall thickening. Where reversal points do not coincide (R–R') both layers possess a Z spiral.*

* It is difficult to ascertain whether or not the points of reversal in subsequent layers of thickening are the same as those of the second layer, but as far as one can determine, this is the case. The fact that reversal points can be distinguished by their extinction position between crossed nicols [3, 9] certainly indicates that definite places where reversals occur are soon established and followed through the subsequent layers of secondary deposition.

lowed to dry. There are indications at times that the innermost layer may differ in the steepness of its spiral structure from the main part of the wall thickening.

Swelling Behavior

When fibers are swollen in cuprammonium hydroxide, the primary wall and winding both play a part in restricting the uniform expansion of the wall thickening. In swollen fibers, there are two types of restricting patterns commonly seen: (1) the well-known beading or ballooning of the fibers and (2) the formation of helical bands (Figure 4C). The ring constrictions which produce the beading are caused chiefly by the primary membrane. The rings stain intensely with Ruthenium red and similar constrictions may be produced by mechanical treatments (Figure 1). When the primary wall is completely removed by mechanical means, beading has never been observed although it is seen in dewaxed and depectinized fibers. On the other hand, the formation of helical bands during swelling is caused chiefly by the winding as evidenced by its orientation.

The restricting action of the outer layers could be produced by two physical factors: (1) the presence of noncellulosic constituents in the primary membrane and (2) the orientation of the cellulose in the primary wall and winding. In depectinized and dewaxed fibers, the restricting action is caused by the fact that the cellulose chains in the outer layer are practically at right angles to the chains in the wall thickening. As the wall thickening expands during swelling, tension is produced on the outer layers. Hess and Trogus [7] have pointed out that it requires a higher concentration of reagent to produce intramicellar swelling when cellulose is under tension. This explains why the winding, in spite of its thinness and solubility in cuprammonia, can prevent the uniform expansion of the main part of the secondary wall. As Hock, Ramsay, and Harris [9] have shown, both beading and helical bands are formed when purified (dewaxed and depectinized) fibers are swollen in cuprammonia. This leads one to the conclusion that although the noncellulosic constituents may aid in the formation of constrictions, these substances play only a minor role.

During the swelling of the fiber, the outer layers rupture. The winding invariably breaks parallel to the direction of its cellulose chains but the primary membrane may tear in various manners. The structure and behavior of these layers may be better understood if the primary membrane is considered to be analogous to a covering of poorly oriented cellophane, whereas the winding resembles a layer of spirally wound threads. During swelling the primary wall frequently ruptures parallel to the orientation of the winding (Figure 4) but it may tear parallel to the striations of the main layer (A′ in Figure 2), or in an uneven manner independent of any orientation (Figure 5B). After the primary membrane and winding rupture they may be rolled back together into a coarse thread or rings by the further swelling of the main part of the wall (Figure 4). In the

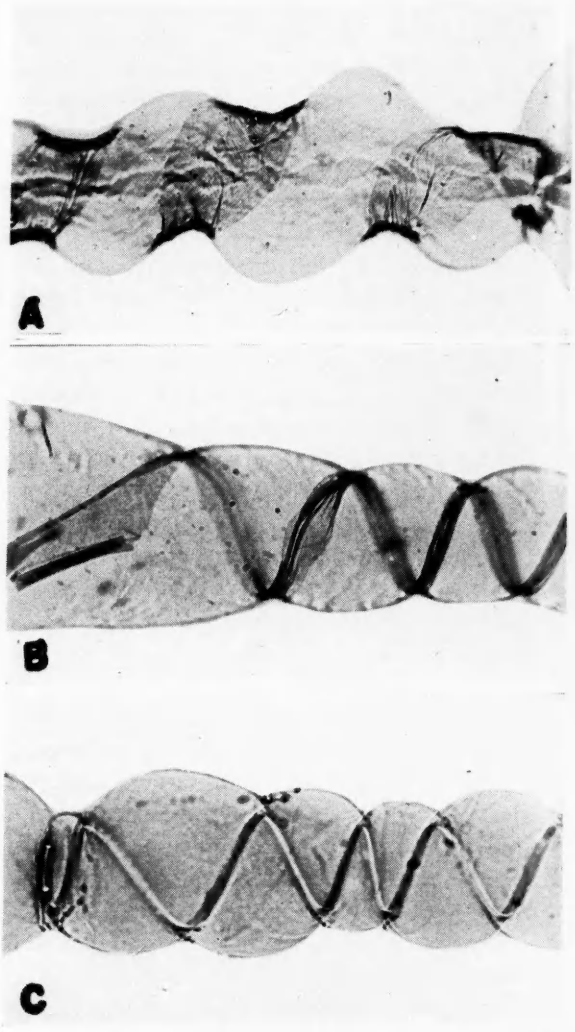


FIG. 4. *Mature but undried cotton, stained with Ruthenium red and swollen in cuprammonia, showing different stages in the formation of spiral constrictions. (A) Primary wall ruptures parallel to the cellulose orientation in the winding and (B, C) folds, forming part of spiral strand. Magnification 400 ×.*

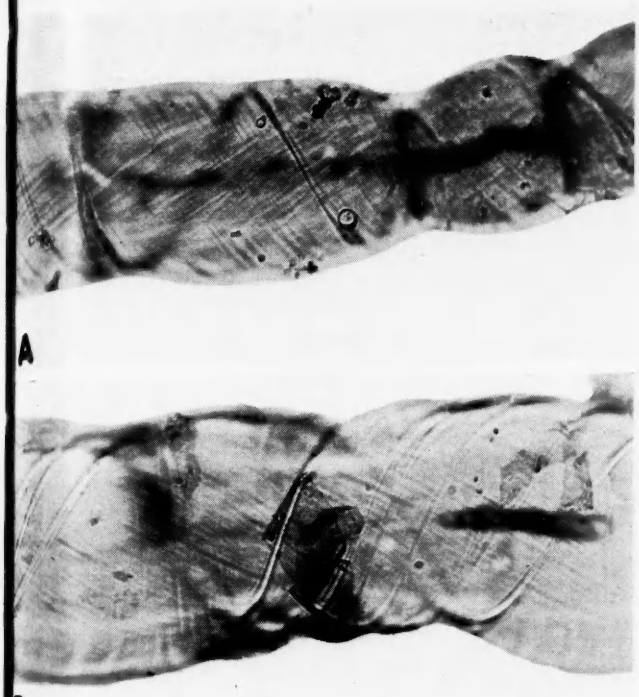


FIG. 5. *Undried Stoneville cotton stained with Ruthenium red and swollen in cuprammonia. (A) Primary wall partially removed but remnant combined in one place with the winding. (B) Primary wall torn in fragments on surface of the fiber. Magnification 650 ×.*

nitrogen dioxide material described by Rollins [12], helical bands are always seen after swelling. The primary wall is apparently affected by the oxidation, offers no resistance to the swelling, and tears parallel to the striations in the winding.

In dried fibers, it is possible that the winding may have a considerably higher percentage of amorphous cellulose than is present in the wall thickening. Berkley and Kerr [5] have shown that in cotton fibers crystallization of the cellulose does not take place in any large amount at the time of deposition but happens chiefly when the fibers dry for the first time. During the initial dehydration, anisotropic shrinkage occurs, similar to the anisotropic swelling described in the preceding paragraphs. The direction of the convolutions that are formed is determined by the spiral structure in the wall thickening, which comprises at least 90 percent of the volume of the fiber. If allowed to shrink freely, the cellulose in the winding would contract at right angles to the cellulose in the wall thickening but this is prevented by the large amount of material in the inner layers. Therefore, the cellulose in the winding must either rupture and crystallize in small patches or become somewhat disoriented during the process of dehydration and therefore remain largely uncrystallized. There is no microscopic evidence that the winding splits away from the wall thickening and buckles, but, other than this, it is impossible to tell at the present time what actually happens during the initial drying.

The Question of Terminology

Hock, Ramsay, and Harris [9] have identified the winding as the outermost layer of the secondary thickening and it has been shown in this paper that the winding is homologous to a layer in wood fibers which had been identified similarly. Rollins [12] has doubted this classification and has considered that the winding could be termed "the inner layer of the primary wall" with equal justification. The distinction between primary and secondary wall was made originally on the basis of development—that is, a physiological distinction [2]. The term "primary wall" has been used to refer to the walls of meristematic cells and their enlarging derivatives, which are characterized at the time of their deposition by a capacity for growth and extension. On the other hand, the secondary wall is composed of supplementary layers deposited after the cell has reached its mature dimensions, when the walls have lost their potentiality for growth and enlargement. After this distinction had been brought forward it seemed probable [1] that pectic substances are restricted to primary walls and the intercellular substance (walls capable of expansion) in most if not all cases.

On the basis of this classification, it is not possible to term the winding as part of the primary wall. The winding is not present during the period of active fiber elongation, and it stains slightly, if at all, in Ruthenium red.* Furthermore, the winding is composed of well-oriented cellulose and possesses reversals, both properties of the secondary wall. The fact that the winding is differentiated from the wall thickening by its orientation cannot be used as evidence that it is a transitional layer if other types of fibers are taken into consideration. In lignified fibers

* When the primary wall is mechanically removed, the winding is almost always unstained in Ruthenium red. At times, evidence of light staining has been observed but it is not possible to say whether this layer contains pectic substances or whether the staining is caused by adhering parts of the primary membrane.

from the stems of various monocotyledons such as bamboo, *Pandanus,* and most of the palms, a layer similar to the winding in orientation is repeated three to six times throughout the thickness of the secondary wall [2, 11].

Rollins [12] has associated the primary wall and the winding and termed them the "sheath" of the fiber. It has been shown that during swelling both layers restrict the uniform expansion of the wall thickening, as a result of differential orientation, and on this basis the two outer layers may well be designated "the fiber sheath." However, from the standpoint of development, the winding is definitely part of the secondary wall. Furthermore, as far as can be determined from present incomplete knowledge, the noncellulosic constituents (the waxes and pectic substances) are restricted or largely confined to the primary membrane;* at least, no evidence has been brought forward to indicate that these substances are present to any extent in the winding. The outer covering of cotton fibers modifies many of its physical and chemical properties, such as wetting, dyeing, swelling, and the ability of fibers to bond with certain substances. To a large extent these properties are modified by the presence of noncellulosic constituents in the primary membrane. Therefore, it would seem desirable to retain the terms "primary wall" and "winding" as distinct entities rather than to associate them because of their behavior in swelling.

The term "winding" has been used in this paper as synonymous with the outer layer of the secondary wall. In one respect this term is unfortunate because all layers of the secondary wall wind—that is, they possess a helical structure. Nevertheless, the term has priority, has no developmental connotation, and is useful in describing a layer in the mature fiber.

* The only known exception is the wax of green lint which is present in concentric layers in the secondary wall. Green lint is a mutant type never found in commercial cottons, although the same green wax constituent is fairly common in linters.

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Correlation of Equilibrium Moisture Data

John C. Whitwell* and Richard K. Toner†

Textile Research Institute and Princeton University

These equilibrium moisture regain studies were initiated in an attempt to extend the data on equilibrium moisture in textile fibers as determined by Wiegerink and others. In the course of the correlation, it became evident that further material of value to the general problem of drying and concentration could be extracted from these and related data by calculations dealing with water solutions and silica gel. The combined information is now presented without an attempt to include the extrapolations and corrections for all of the textile data.

The data are correlated by the use of Othmer charts. The constant regain lines on these charts are extended statistically to a common point of intersection characteristic of any one fiber in any one process of sorption or desorption. The location of this common point is interpreted in light of the restriction of the water molecule on the fiber and the relative swelling property of the material. Regions of moisture regain are found which give conclusive evidence of pure adsorption uncomplicated by swelling.

Another paper, "Statistical Methods for Equilibrium Moisture Correlations," by Professors Whitwell and Toner and Mr. P. J. McCarthy, will appear in the July issue.

Introduction

Interest in drying may be divided between the actual removal of water by such means as steam-heated drums, hot air, or infra-red radiation, and the equilibrium moisture of materials under various relative humidity and temperature conditions, the latter as a means of providing data for control and for drier design. It is the purpose of this paper to study these latter relations, particularly with respect to data for textiles.

Despite the emphasis upon equilibrium regain data for textile fibers, all relationships noted are general in character, applying basically to drying and concentration processes. Silica gel, characterizing "inelastic" gels, and solutions as opposed to polymerized bases for water, will be shown to follow generalizations applicable to, and specifically developed from, textile data.

History

Hartshorne [3] was among the first to make a systematic study of the moisture regain of textiles under various conditions, although the first published work on the subject appears to be by Schloesing [16]. Hartshorne called attention to the importance of its history on the moisture relations of the fiber and noted the existence of a hysteresis effect which, however, he attributed to the time lag in the attainment of equilibrium when it is approached from opposing sides, believing that only a single sorption curve actually exists. He prepared extensive tables and equations of moisture regain versus relative humidity for cotton and worsted, with both the equations and the tables based upon limited experimental data and the assumption that each molecule of water is added to the fiber in the same fashion as all those preceding and following it. It is not to be expected that Hartshorne's results will be in good agreement with other experimental data since these assumptions are invalid. The knowledge that true hysteresis does exist in textile fabrics has been available since 1915 [14], but only since 1924, when Urquhart and his coworkers [20, 21, 22, 23, 24, 25, 26, 27, 28, 29] began to publish the results of their research on cotton, has a true insight into this behavior been possible.

Necessity for Correlation

It is unnecessary to survey the history of this work in further detail since this has recently been done by Carlene [1], but it would be well to review briefly

* Director of Research, Textile Research Institute, and Professor of Chemical Engineering, Princeton University.
† Textile Research Institute Staff and Assistant Professor of Chemical Engineering, Princeton University.

the reasons for the present investigation. In spite of the excellent experimental work of Wiegerink [31], which is the most exhaustive yet published for the temperature range of 35°C to 150°C, inspection of his results shows two deficiencies: incompleteness in the lower end of the moisture-regain-versus-relative-humidity plot, which is of particular importance at low temperatures, and occasional disparity between forms of isotherms, indicating unavoidable experimental inaccuracies, and thus the necessity of adjusting the curves to correct for these errors. With the exception of the work of Neale and Stringfellow on cotton [6], there are no useful experimental data for a very low moisture regain for any fiber. It therefore becomes desirable to extend experimental curves to this region.

In addition to these problems, there is the absence of data on new fibers such as nylon, high-tenacity rayon, and the newer synthetics. Then, there is the difference among fibers of the same type due to their history—for example, cotton spun, woven, sized, dyed, etc. It is evident that if a basic correlation of existing data were possible, especially if this correlation could be proved to have a sound theoretical basis, the textile research engineer would find it of considerable value. It is also conceivable that these results would be applicable to nontextile materials.

Choice of Data

A considerable mass of consistent data on a variety of materials must be available to serve as a basis for a general correlation. For this reason, the data of Wiegerink [31] were chosen, supplemented, for cotton, by those of Urquhart and Williams [28] and those of Neale and Stringfellow [6], the last to provide a test of the method at very low regains. By using the data of Urquhart and Williams, the method of correlation employed could be checked to 20°C, which is 15°C below Wiegerink's lower limit. Although Wiegerink covers raw, "purified," and mercerized cotton, raw and degummed silk, carpet and clothing wool, and cuprammonium, acetate, and viscose rayon, he did not study any of the synthetic fibers. Unfortunately, data for these materials are either unavailable or so incomplete that they cannot be included in this publication. Certainly two, and preferably not less than three, different isotherms are essential. If only two are available, the experiments must represent a most exact and consistent technique. If this condition does not hold, analysis is unlikely to be successful, as was discovered in an attempt to correlate data at two temperatures only for high-tenacity rayons.

Wiegerink's desorption data are the more complete; in many cases those on sorption meet only minimum requirements for reliable correlation, the experimental points being fewer in number than those on desorption for similar material.

Definition of Terms

As used in this article, the term "regain" has the standard textile meaning of percent moisture on the dry basis. To indicate gain and loss of moisture by the fiber, the terms "positive sorption" and "negative sorption" are desirable, but in deference to common practice "desorption" will be employed for moisture loss. However, "adsorption" must be avoided, as this term applies strictly to only one portion of the positive sorption process. The term "sorption" will therefore be used for the gain of moisture by the fiber.

Objectives

The purpose of this communication is to provide a satisfactory correlation method for existing data, thereby eliminating minor inconsistencies, and to compare the knowledge so gained to other polymeric substances and to solutions. Succeeding papers will give in detail the mathematical methods employed, for the benefit of those who wish to extend this type of calculation to data not covered in these reports, and, finally, correlations by this method for natural and synthetic fibers for which adequate data are available, with directions for the construction of equilibrium moisture charts from a minimum of experimental data on either a fiber for which a prototype has been studied or for one which is entirely new in character.

Theoretical Basis for Correlation

Correlation Method

The integrated form of the Clausius modification of the Clapeyron equation has frequently been used in attempts to correlate data on moisture regain. These equations, written for a pure substance, are:

$$\frac{dP^\circ}{dT} = \frac{\lambda}{T\Delta v} \text{ (Clapeyron equation);} \quad (1)$$

$$\frac{dP^\circ}{dT} = \frac{P^\circ\lambda}{RT^2} \text{ (Clausius modification of equation (1)).} \quad (2)$$

Integrated form of equation (2):

$$\log P^\circ = -\frac{\lambda}{R}(1/T) + \text{Constant.}^* \qquad (3)$$

Equation (2) is obtained from equation (1) by assuming that the specific volume of the liquid, v_L, is negligible in comparison with that of the vapor and that, from the simple gas law, $v = RT/P$. Both assumptions may be shown to be valid in all cases cited in this paper.

Previous work on textile correlations has generally been based upon equation (3) [6, 28, 30], with ΔH, the heat involved in the process of transferring water between the vapor phase and the condensed phase on fiber, replacing λ. Another method was recently proposed [15], but it is of such limited scope and questionable accuracy that it need not be considered. Wiegerink [31] has used an empirical representation of low regain versus $1/T$. The main objection to such a method lies in the curvature of each line representing relative humidity as the parameter. As a result, if straight lines are drawn through the upper and lower temperature regions of the experimental points, their straightness has no theoretical meaning and they are a convenience only. It is particularly important that *no* significance be attached to the temperature of intersection; some was implied in Wiegerink's original article.

In correlations based upon equation (3) it has been uniformly assumed that a line whose coordinates are log P and $1/T$ will be straight. This assumption would be true only if ΔH were a true constant with respect to temperature. That such is not the case is a well-known fact, recognized by all of the investigators who have used the equation. The assumption was necessary so that the actual curvature existing in the temperature range of their experiments might be neglected in calculations. Such assumptions frequently prove to be fact, but in at least one of the above cases [31] an exceptionally wide temperature range was involved (35°C to 150°C).

Since in the present work the same temperature range was involved, it was obvious that the log P-$1/T$ method was unsuitable. Consequently, another method of representing data derived from the same, fundamentally correct, basic equation (equation (2)) was used. Othmer [7] first adapted this basic relation for representing the vapor pressure of pure liquids and subsequently [8, 9, 10] the vapor pressures of one component of a solution, moisture relations of paper, reduced conditions for high pressures, etc. To the authors' knowledge, no one has previously attempted so to represent equilibrium moisture relations for textile fibers.

Othmer's method, depending upon equation (2) above, makes the same assumptions noted at that point, assumptions which may be proved reasonable in the range involved. Equation (2) is written twice, once for pure water and once for water vapor over the material in question (in this case, fiber):

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2} \qquad (4)$$

Dividing equation (4) by equation (2) and considering a single temperature,

$$\frac{dP}{dP^\circ} = \frac{P\Delta H}{P^\circ\lambda}. \qquad (5)$$

Rearranging the terms gives

$$\frac{dP/P}{dP^\circ/P^\circ} = \frac{d\ln P}{d\ln P^\circ} = \frac{\Delta H}{\lambda}. \qquad (6)$$

Integrating equation (6),

$$\log P = \frac{\Delta H}{\lambda}\log P^\circ + \text{Constant.} \qquad (7)$$

As long as the data for vapor pressures of water over fibers and over pure water are compared at the same temperatures, this equation holds, and a plot of log P versus log P° will yield straight lines if the temperature dependences of ΔH and λ are similar. For fibers it is apparent that lines on such coordinates

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* SYMBOLS:

ΔH—heat effect of either sorption process, calories per gram molecule of water
$\Delta H'$—heat effect of either sorption process, calories per gram, excluding latent heat
ΔH_a—heat of adsorption, calories per gram molecule of water
ΔH_s—heat of swelling, calories per gram molecule of water
ΔH_x—undesignated heat effects, calories per gram molecule of water
MR—moisture regain
P—vapor pressure of water over fibers, Si-gel, solutions, etc., mm.Hg
P°—vapor pressure of pure water, mm.Hg
R—universal gas constant
ΔS—entropy change occurring during phase change
ΔS°—entropy change occurring during phase change at a reference state
T—temperature, degrees Kelvin
s—slope of Othmer line
v—specific volume of the vapor phase
v_L—specific volume of the liquid phase
Δv—difference in specific volume between condensed and vapor state ($v - v_L$)
$\bar{x}$—average of any set of figures
λ—latent heat of evaporation of water, calories per gram
σ—standard deviation for figures to which $\bar{x}$ applies

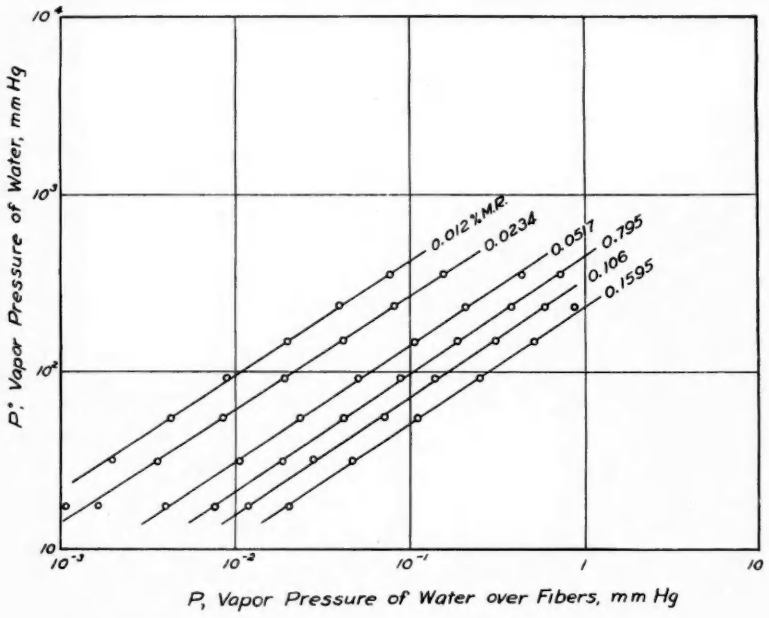

FIG. 1. *Data of Neale and Stringfellow for low regain on washed cotton in sorption, plotted as indicated by equation (7).*

must represent one moisture condition only (that is, lines of constant regain are to be plotted); otherwise, relationships established by moisture-to-fiber positions will vary and no correlation could be expected.

Figures 1, 2, and 3 are based upon equation (7).* On each figure there are lines of constant regain, and on Figures 2 and 3 a reference water line is indicated. This line would be obtained by plotting the data for water against itself (that is, log P° versus log P°). Straightness of the individual lines of constant composition indicates a reasonable verification of the one assumption involved (similar ΔH and λ temperature dependences in the range of the data).

If experimental techniques are adapted to lower temperature measurements, these new data will provide evidence of the lower temperature limit for the correlation. Since Othmer found no lower limit of applicability down to phase change, and since the data of Urquhart and Williams correlate well, temperature is not a current source of worry. Furthermore, the data of Neale and Stringfellow show straight lines; hence, there seems no reason to question the suitability of the method in regions of low moisture regain.

Common Point

Examination of Figures 1, 2, and 3 shows that the lines on all except Figure 1 indicate a progressive change of slope with water content. Thus, such casual inspection indicates that it is possible for all the lines representing any one material to intersect in a single point, which shall be designated as the "common point."

Statistical methods [18] may be adapted to show the probability of the existence of a common point. The details of this method will be presented in a later paper. Of all the data studied, only those for cuprammonium, viscose, and clothing wool, all in desorption, and for sodium chloride solutions do not give at least fair evidence of intersection. Since twenty-one different textile systems were studied and only these four failed to show evidence of intersection, it is assumed that the failure may be charged to experimental error rather than to departure from the assumption of the common point.

Location of Common Point

While it is convenient to represent the lines on the Othmer plot as linear both in the region of the data and in the high-temperature extrapolations, their over-all straightness has been noted to be dependent upon similar variation with temperature of both ΔH and λ. At high temperatures a theoretical distinction can be proved.

The "common point" is therefore only a convenience representing extension of the statistically straight lower portions of the Othmer charts to intersection. However, if it can be predicted, its location is of value in estimating data for materials whose moisture properties have not been experimentally investigated.

The following discussion will propose that the location of the common point may be broken down into: (*a*) the horizontal displacement from the reference water line, defined by the value of log P/log P°, and (*b*) the vertical distance, as defined by its component value of log P°. It will be proposed that the horizontal displacement is characteristic of the restriction of positions to which water may attach itself

* Coordinates reversed to adapt data to commercial graph paper.

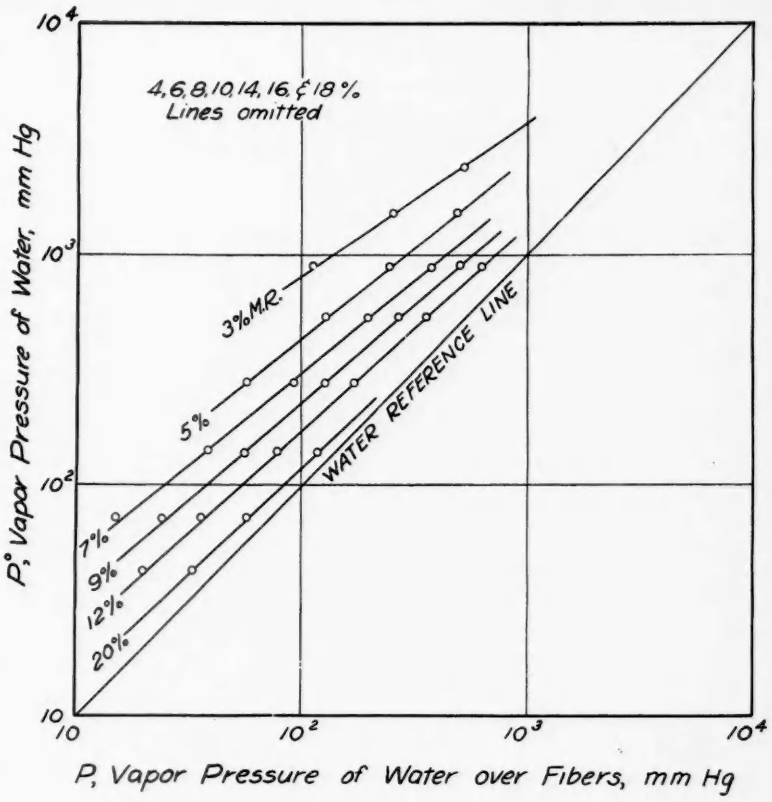

FIG. 2. *Data of Wiegerink for cuprammonium rayon in desorption, plotted as indicated by equation (7).*

on the fiber and that the vertical distance is an inverse function of the swelling property.

Horizontal Position

The probable horizontal position of the common point may be predicted by rewriting the Clausius relation and showing that, as T approaches infinity,

$$\ln \underset{(T\to\infty)}{P} = \Delta S/R. \qquad (8)$$

Similarly, at high T,

$$\ln \underset{(T\to\infty)}{P^\circ} = \Delta S^\circ/R, \qquad (9)$$

where ΔS and ΔS° are entropy changes of water from the condensed to the vapor phase; therefore

$$\frac{\ln P}{\ln P^\circ} = \frac{\Delta S}{\Delta S^\circ}. \qquad (10)$$

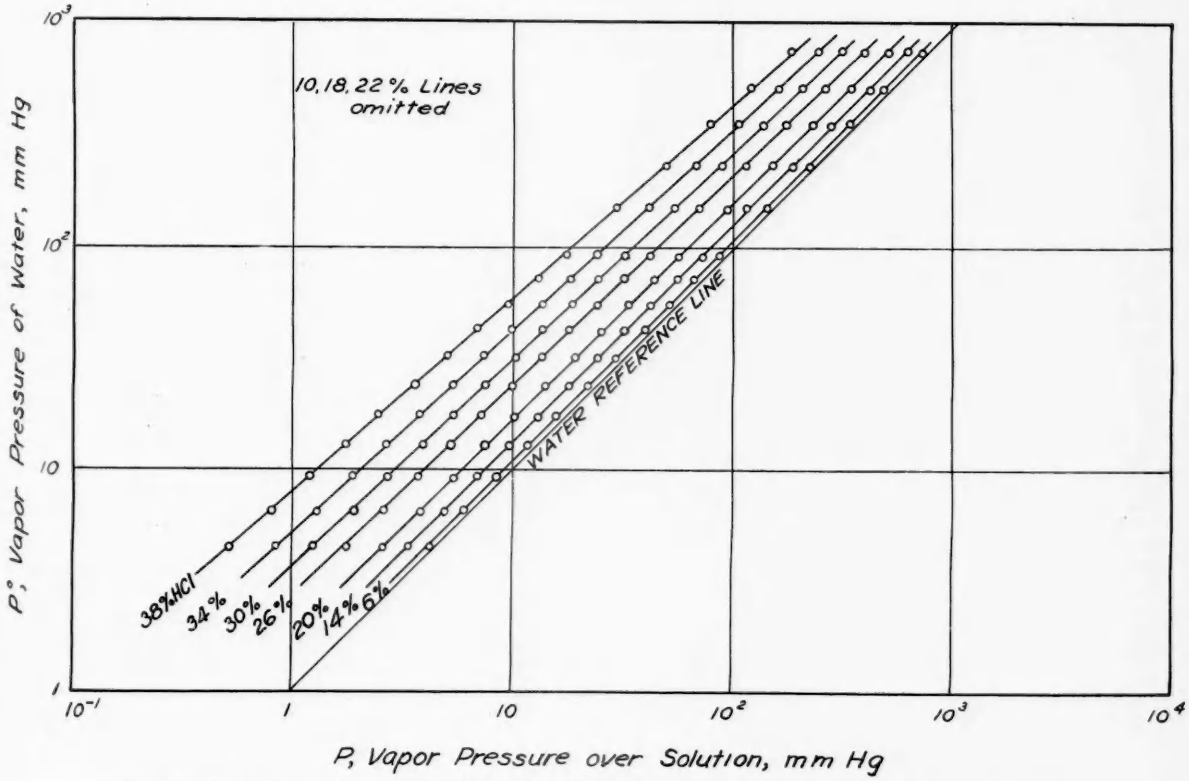

FIG. 3. *Data from* International Critical Tables *for the system hydrogen chloride-water, plotted as indicated by equation (7).*

FIG. 4. *Data for cuprammonium rayon plotted as recalculated from statistical determination of the common point.*

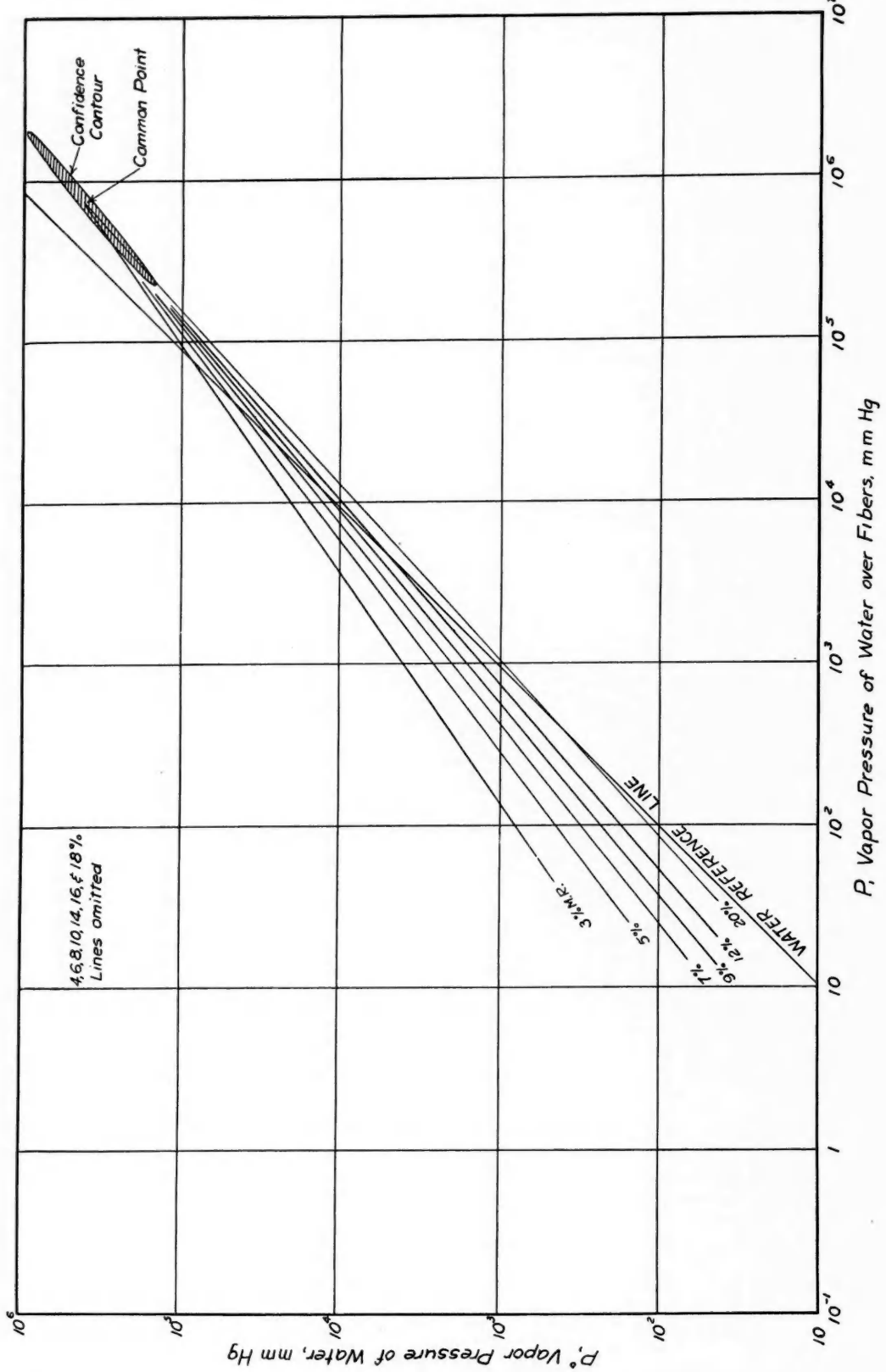

FIG. 5. *Data for hydrochloric acid plotted as recalculated from statistical determination of the common point.*

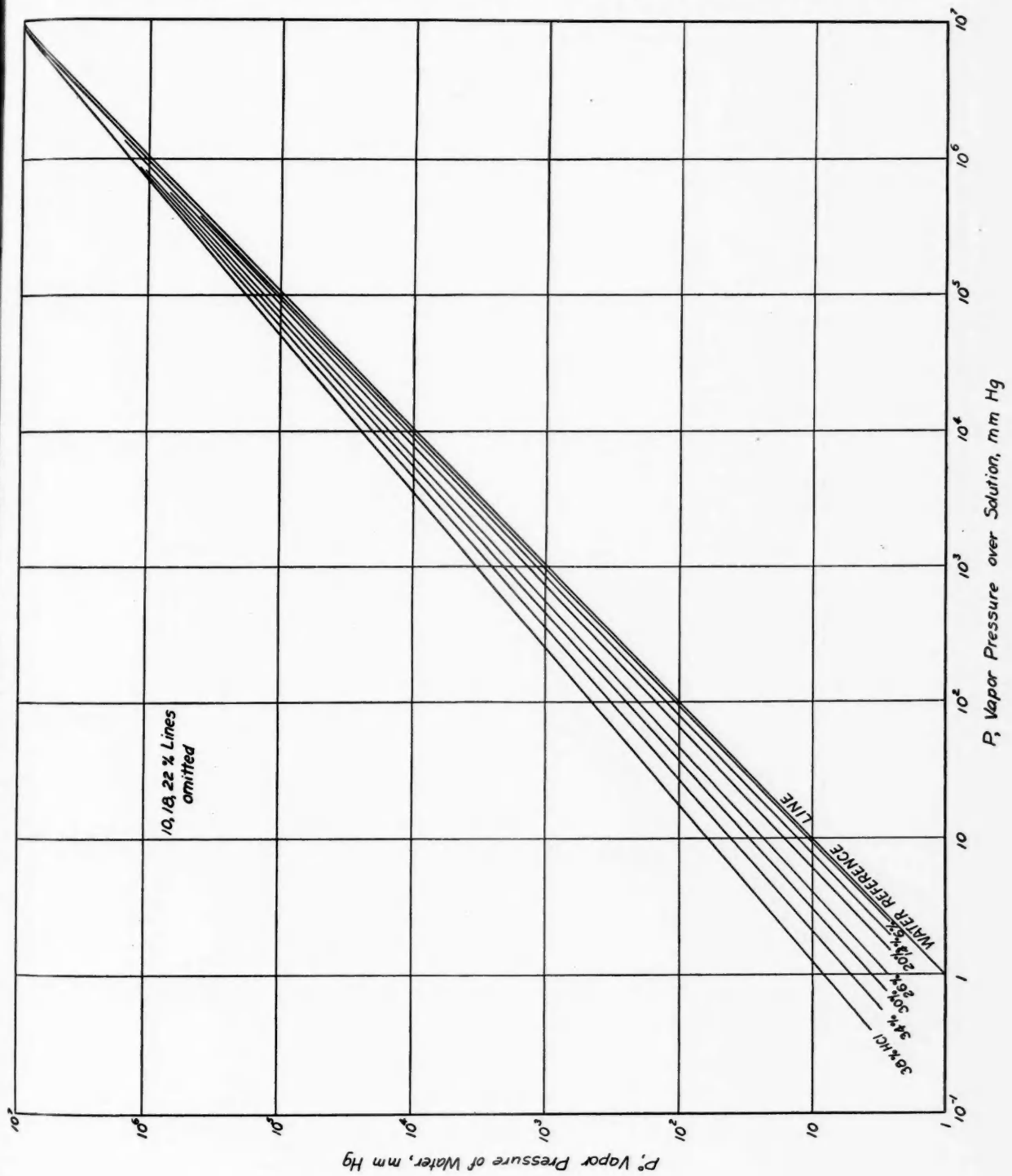

TABLE I. Log P/log $P°$ AT COMMON POINTS

Material	log P/log $P°$ Sorption	Desorption
Raw cotton	1.044	1.027
Purified cotton	1.034	1.033
Mercerized cotton	1.034	1.034
Raw silk	1.043	1.036
Degummed silk		1.046
Clothing wool	1.052	1.048
Viscose rayon	1.047	1.039
Cuprammonium rayon	1.023	1.050
Acetate rayon	1.042	1.047
Average	1.040 ± 0.0033	1.040 ± 0.0025
Silica gel		1.039
H_2SO_4-H_2O	0.987	
HCl-H_2O	0.994	
NaCl-H_2O	0.998	
Average	0.993 ± 0.003	

Comparative values of $\Delta S/\Delta S°$ may be predicted from a knowledge of the process. In descriptive terms the results of such predictions, based on the Eyring [2] theory, may be summarized as follows. As the temperature rises and the vibrational energy of the water molecule is increased, it moves rapidly among these positions, eventually being vaporized. In the case of water on fibers, the choice of positions is much smaller than with water, and at high temperatures the molecule has a greater tendency to vaporize as its energy is increased than it does from water. In other words, a temperature may be expected at which the vapor pressure over the fiber is greater than that over water itself. When the vapor pressure lines cross the water line, this condition is realized.

The higher the water content, the sooner the line would be expected to cross the reference water line, as the positions on the fiber are already more limited.

Qualitatively, the above theory is seen to be obeyed by the general character of the family of curves shown in Figures 4 and 5. The same situation would not be predicted to hold in the case of the water solutions.

Results. Statistical calculations undertaken to show this effect are summarized in Table I and are represented by Figures 4 and 5, which are characteristic of all fibers and of water solutions studied. The total group of systems studied included: in desorption only, silica gel [19]; in sorption only, data on cotton at low regain by Neale and Stringfellow [6] and data on cotton by Urquhart and Williams [28]; and in both sorption and desorption, raw cotton, purified cotton, mercerized cotton, raw silk, degummed silk, clothing wool, carpet wool, viscose rayon, cuprammonium rayon, and acetate rayon [31]. In addition to these fiber data, the systems salt-water, hydrogen chloride-water, and sulfuric acid-water have also been analyzed on the basis of data from the *International Critical Tables* [4] and Perry [13]. Subsequent discussion is based upon all of these data.

In Table I are tabulated the log P/log $P°$ data for fibers in both sorption and desorption, with the summations representing the average plus-or-minus standard error.

The comparative values are too striking to be overlooked. Not only are the sorption and desorption values identical for fibers as a group, but silica gel is of the same character, whereas solutions are completely different. All polymerized materials show the same ratio, whether they are of the inelastic gel or the elastic type. (Fiber is the latter, according to Peirce [12]; Si-gel, the former.) All "monomeric" materials, such as solutions, have a ratio of essentially 1.00. It is probable from these results that, within the limitations of the method, physical effects are more important than chemical bonding. Thus, although the qualitative theory predicted for the restriction of the water molecules may be satisfactory, the restriction may be explained as the physical one imposed by the mechanical forces required to force apart the molecular fibrils rather than the chemical one of bonding positions. This statement is equivalent to attributing the restriction to the bonds holding the individual molecular chains together rather than to those holding the water to a fiber molecule. Such effects do not exist in the case of solutions, so that intersection is on the water line and the vaporizing molecules act normally.

The value of log P/log $P°$, calculated from Taylor's data on silica gel, is 1.039, as noted in Table I. These data were expected to illustrate the difference between this "inelastic gel" and the elastic-gel-like textile fibers. It is apparent that this ratio classifies the inelastic gel in the same category as fibers. The important fact seems to be that the polymerization state is more important than the supposed character of the gel.

Vertical Position

The change in slope between the adjacent constant regain lines will essentially determine the vertical

position of the intersection. This "vertical" distance can be measured either along the water line or as the value of either the true vertical or horizontal component (that is, log P or log P°). For convenience, the distance will subsequently be specified by its component on the P° axis. Errors introduced by variation from 1.0 of log P/log P° at the common point are sufficiently small to be negligible.

In considering the change of slope from one line to another, the interpretation of the physical significance of each slope is important. If the slopes of any two moisture regain lines of composition A and B are considered, it is obvious that a material with the greatest difference between these two slopes will have the lowest common point (lowest P° at intersection). The slope is a function of ΔH, the heat effects of the process of the change of water from the condensed state on the fiber to the vapor state (or vice versa), since

$$\text{slope} = \Delta H/\lambda = s. \tag{11}$$

Moreover,

$$(s - 1) = \Delta H/\lambda - 1 = \frac{\Delta H - \lambda}{\lambda}. \tag{12}$$

At any temperature λ is known, so that ΔH or $(\Delta H - \lambda)$ may be calculated. Furthermore, ΔH may be broken into its component parts, as follows:

$$\Delta H = \Delta H_a + \Delta H_s + \lambda + \sum \Delta H_x, \tag{13}$$

where ΔH_a is the true adsorption heat, ΔH_s is the swelling heat only, and $\sum \Delta H_x$ is the sum of *all* other heat processes, whether or not they can be evaluated. Thus, from measurement of the slope, calculation of heat effects would show that

$$(s - 1)\lambda = \Delta H_a + \Delta H_s + \sum \Delta H_x. \tag{14}$$

It is on this summation of heats that the vertical position of intersection depends. The greater the heat per molecule, the greater the slope change per unit change of concentration and the lower the value of log P° at intersection.

If in equation (14) it can be assumed that ΔH_s is the predominant heat effect, with ΔH_a and $\sum \Delta H_x$ negligible in comparison, it is apparent from the preceding discussion that the value of P° at intersection is a function of the swelling property of the fiber. This assumption is hereby made; errors involved will be noted later.

No extended discussion of the calculated ΔH values will be included. However, there is excellent agreement with the values reported by Neale and Stringfellow from their calculations. Values for "purified" cotton are shown in Figure 6. Comparison with reports of other investigators also shows the values to be satisfactory.

It must be realized that the proper basis for study of ΔH effects is the unit of fiber. Thus, although the slopes decrease, the total heat per gram of fiber increases, since

$$\text{Heat evolved (or absorbed) per gram of fiber} = (\Delta H')\ (MR).$$

Here $\Delta H'$ is expressed as calories per gram of water, excluding latent heat, with λ in the same units, and MR is defined as grams of water per gram of dry fiber. The curves may be represented qualitatively, as in Figure 7. Figure 7B (right) is of the usual integral heat form.

Results. Data on the swelling of fibers in water are scanty. The technique of its measurement is neither well worked out nor precise. Authorities who have summarized the data available are Ott [11], Carlene [1], and Smith [17]. Their figures are shown in Table II, in which swelling is reported as percent increase in cross section. Since the swelling of fibers is predominantly lateral rather than longitudinal, this representation is also essentially equivalent to volumetric swelling.

While the swellings reported by these authorities do not show perfect consistency, an attempt to average and to list them in descending order is shown in the first column of Table III. Comparison with the results obtained from calculation of desorption data is indicated in the second column, while in the third column is the P° value at intersection. Silk, which has very low values of P° in both the degummed and the raw state—so low that its proper calculated position is that of most potent sweller—is the only material which fails to agree reasonably well with the initial hypothesis.

Characterization of swelling from sorption data is not quite so consistent as that from desorption data. However, in general the sorption data available were not so extensive as those for the reverse process and therefore less reliable.

While agreement with the theoretical proposal is qualitatively good, it is naturally complicated by other heat effects, as can readily be seen from equation (13). If ΔH_a values for different fibers are not proportional to ΔH, which they undoubtedly are not, there will be some masking effect of the relation of

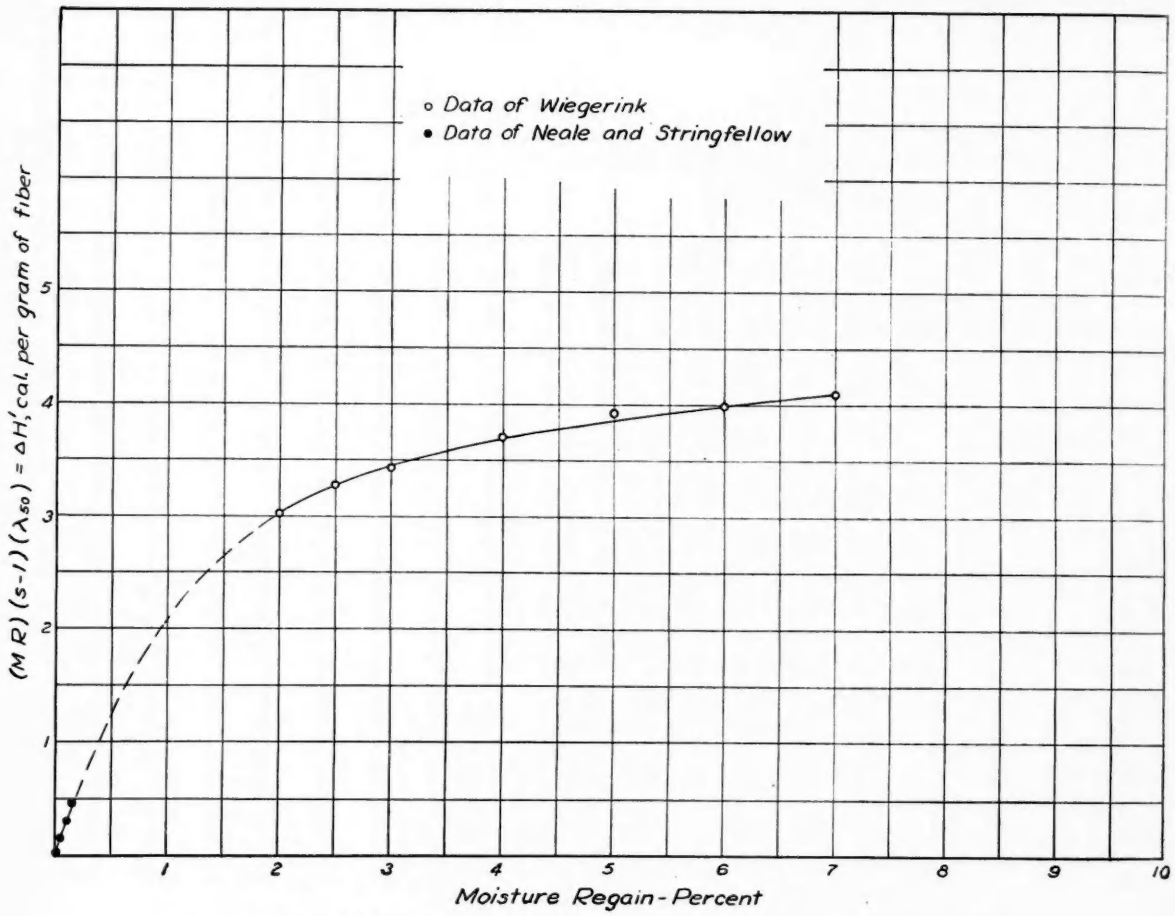

FIG. 6. *Heat effects noted experimentally in sorption of water by washed cotton.*

ΔH_s to the slopes. It is either to such an effect, or to a poor experimental swelling value for silk, that misplacement of this material in Table III is to be attributed; the former is the more likely to be responsible.

At the bottom of Table III are listed values of $P°$ at the common point for the Neale and Stringfellow data on cotton at extremely low moisture regains and for four solutions. The solutions, which should present none of the complications of heat of adsorption experienced with fibers, also show interesting correlation with "swelling." In solutions "swelling" is a departure of the total volume from additivity of the volumes of the individual components (that is, departure from ideality). Calculations indicated that hydrochloric acid solutions depart more from the ideal than do sulfuric, which might be expected from the very high heats of solution. Thus, the three water solutions fall in the order that would be predicted. The ideal solution is based upon toluene,

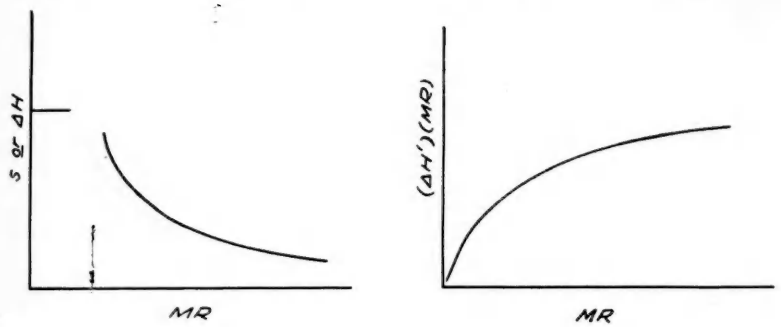

FIG. 7. *ΔH versus moisture regain. (Diagrams not drawn to scale.)*

TABLE II. SWELLING, PERCENT VOLUME INCREASE

	Ott	Carlene	Smith
Viscose, reg. tenacity	73.9	82	45
Cuprammonium	67.8	99–134	—
Cotton	44–49	44	44
Wool	—	38	32
Silk	—	35, 41	30
Acetate, reg. tenacity	—	19–30	11
Triacetate	6.0	4–6	—
Nylon	—	—	slight
Vinyon	—	—	0

with a vapor pressure of the second component calculated so that Raoult's law is applicable. This binary then being ideal, perfect additivity should exist and the lines should not intersect. As noted in Table III, all the lines are parallel.

The data for silica gel indicate a P° at the intersection of 10^9 mm. Hg. The inelastic gel therefore shows definite swelling, not so pronounced as that of natural fiber but distinctly in the range of that of acetate. This similarity is likewise shown by the ratio of log P/ log P° discussed above. It therefore seems likely that all gels should be considered to be similar in character, differing only in degree.

The data of Neale and Stringfellow were taken between 0.01 and 0.16 percent regain. Therefore they can reasonably be assumed to fall entirely in the true adsorption region. If this is the case, each water molecule should go onto the fiber in exactly the same manner as every other molecule, producing the same amount of heat per molecule and resulting in parallel regain lines. The case is similar to that of the ideal solution and the lines again have been shown to be statistically parallel.

Since the heat effects on fibers in normal regions are more complicated than those of solutions, a system of breaking these heats into their individual components would be most desirable. The data of Neale and Stringfellow seem to provide the key to such a separation provided the term $\sum \Delta H_x$ is relatively small or nonexistent. These data indicate that vapor-pressure studies in low moisture regain regions will show the region of parallelism of regain lines. If carried sufficiently far, they should also show the limit of this parallelism, which point is equivalent to the introduction of swelling effects. Unfortunately, the data on sorption of moisture on cottons do not overlap. Neale and Stringfellow's work ends at 0.16 percent moisture regain and Wiegerink's and Urquhart's begins at above 1 percent. It is in the region intermediate to these experimenters' data that the change from pure adsorption to adsorption-plus-swelling occurs. Naturally, it is possible to extrapolate the known lines on different types of diagrams, but an accurate approximation of the position of change cannot be so determined. Figure 7 shows the data for cotton. For a complete study, such low regain data are necessary for other fibers. The authors hope to be able to produce some of these data.

It should be noted that it is probable that as many as three distinct regions exist, one pure adsorption, another pure swelling, and a third a mixture of the other two interposed between the two pure cases. Current data afford no means of distinguishing the

TABLE III. DECREASING SWELLING ORDER

Experimental	*Calculated Desorption*		*Calculated Sorption*	
	Material	P°	Material	P°
	Raw silk	3.16×10^4	Cuprammonium rayon	1.51×10^5
Mercerized cotton	Degummed silk	6.46×10^4	Raw silk	1.78×10^5
Viscose rayon	Mercerized cotton	1.41×10^5	Mercerized cotton	2.00×10^5
Cuprammonium rayon	Viscose rayon	1.59×10^5	Cotton (U. and W.)	4.34×10^5
Cotton	Purified cotton	3.16×10^5	Clothing wool	7.94×10^5
Wool	Cuprammonium rayon	3.63×10^5	Viscose rayon	10.0×10^5
Silk	Clothing wool	4.17×10^5	Purified cotton	14.1×10^5
Acetate rayon	Acetate rayon	1.58×10^9	Acetate rayon	1.58×10^{12}
	Cotton (N. and S.)—low regain—lines parallel			

Solutions

Material	P° mm.Hg
HCl-H_2O	1.0×10^7
H_2SO_4-H_2O	3.16×10^7
$NaCl$-H_2O	1.0×10^{20}
Ideal solution	∞ (i.e., parallel)

moisture regain boundaries. It is therefore conceivable that some of the low regains used in calculating common points are really not in the pure swelling region. Such lines would carry too much weight in establishing the common point. In the four cases which showed no evidence of intersection, this condition is definitely expected to have occurred. Low moisture regain data would elucidate this point.

Relation Between Sorption and Desorption

It seems reasonable to assume that some relation should exist between common points in sorption and desorption. The calculated ratios of the log P° values for the two processes are listed in Table IV. These results indicate that P° for sorption is, on the average, greater than the equivalent value for desorption and that the relation is calculable. Such data are of the utmost importance in predicting regain for previously untested fibers. Note that the values of $\bar{x} \pm 3\ \sigma$ show a range of 0.755 to 1.456. Thus, no values are excludable if the sample may be considered large enough for statistical treatment.

TABLE IV. RATIOS OF log P° VALUES

Material	log $P^\circ_{sorp.}$/log P°_{desorp}	
Mercerized cotton	1.025	
Viscose rayon	1.154	
Cuprammonium rayon	0.932	$\bar{x} = 1.105$
Purified cotton	1.118	$\sigma = 0.117$
Raw cotton	1.072	
Clothing wool	1.050	
Raw silk	1.166	
Acetate rayon	1.326	
	Average = 1.105 ± 0.0413	

Fiber History

In any study of fiber properties the characteristic dependence of properties upon fiber history must be appreciated. Fiber history may be defined as any condition from or during the growth of the seed to the moment of measurement which may affect the molecular character and configuration within the molecule. While such a statement is primarily a definition for the condition of a vegetable fiber, its inclusiveness is the main point of importance and may readily be properly defined for an animal or synthetic fiber.

Regardless of origin, the condition of micellar arrangement, molecular chain lengths, proportions of crystalline and amorphous regions, and even chemical structural modifications are dependent upon the previous history of the sample. If any or all of these properties vary through growing conditions, climatic variations, ginning practice, milling operations, warp desizing treatment, bleaching, or a host of other possible variables, the physical properties will be affected. Equilibrium moisture regain is one of these properties. Thus, the data here presented and correlated are known to be characteristic only of those samples on which the various investigators worked. For general value, the correlation must be extendable to all fibers of the same class (cotton, silks, wools, etc.). Although this extension has not been included in this publication because of lack of space, it will be the subject of another paper which will shortly be offered.

Summary

1. Data for equilibrium regain on fibers may be well represented by lines of constant regain on an Othmer-type plot.

2. The constant regain lines may be extended to a "common point" of intersection by statistical calculation.

3. The location of the common point may be interpreted and predicted with reasonable assurance in terms of the ratio log P/log P°, and the relative swelling property of the material may be studied.

4. The location of the common point for the sorption process may be related to that for the desorption process by multiplying by the factor 1.10.

5. Heat effects for the sorption and desorption process may readily be calculated from the slopes of the regain lines on the Othmer plots.

6. Low regain lines on the Othmer plot are parallel, indicating a true adsorption process. If the limits of this parallelism were known, the heat effects in adsorption could be differentiated from those of swelling.

7. Data on fibers may be compared with data on solutions, which also give good results on Othmer-type plots.

8. There is no distinction in moisture characteristics between "elastic" gels as represented by all fibers and "inelastic" gels as represented by silica gel.

9. Solutions differ from gels in that the restriction of bonding does not occur, and the common point has the ratio log P/log $P^\circ = 1.0$.

Acknowledgment

The authors are indebted to Mr. P. J. McCarthy of the Princeton University Mathematics Department, who assisted in the statistical analysis of the data; to Professor Henry Eyring, who helped to clarify some of the theoretical material presented; and to Miss Carol Bowen, who performed the numerous essential computations. To Mr. Giles E. Hopkins they owe much for his sound advice and unfailing encouragement.

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Determination of Statistical Control and Related Factors in the Performance of Breaking-Strength Testing of Fabrics

Norman B. Edelman[1]

A study of test results obtained by 50 operators, considered as a group, on measuring the breaking strength of uniform twill fabric following a widely accepted "grab method" technique showed 26 percent of the operators to be out of statistical control.

It was found that those operators whose tensile testing was out of control had not met the two requirements of considerable experience and continual performance in textile testing.

Jaw breaks, which constitute about one-third of all the breaks performed, are shown to give more variable strengths and definitely lower average strengths than acceptable breaks, indicating that the jaws of the test machine contribute a weakening effect on the fabric and that jaw pressures should be known and regulated. Good operators (those in control) get practically the same number of jaw breaks as those out of control. A good operator will not necessarily get higher breaking strengths, or better types of breaks.

Introduction

The present paper is based on a study [2] conducted at the Philadelphia Quartermaster Depot, which was designed to illustrate statistical control in breaking-strength testing of textile fabrics and was performed in accordance with Federal Specification CCC-T-191a. The survey was intended to determine whether: (1) any person who has had some experience in performing "breaks" should be permitted to perform these tests when the occasion arises or whether performance of tensile-strength tests is a highly specialized technique for which only a select group is eligible; (2) there is justification in the belief that "jaw breaks" are invalid and should be deleted from evaluations of the strength of a fabric; (3) the number of "jaw breaks" obtained can be used to evaluate the skill of an operator; (4) the kind of breaks—that is, excellent, good, or fair, as defined in the report—is related to the skill of the operator.

[1] Technologist, Philadelphia Quartermaster Depot.

[2] Report submitted by the Director of Research and Development, Philadelphia Quartermaster Depot, to the Military Planning Division of the Office of The Quartermaster General.

Procedure

Fifty laboratory workers [3] were selected to perform tensile tests on a given piece of cloth cotton,[4] Uniform Twill Type IV, O.D. No. 7. The subjects were selected on the basis that: (1) they continually performed tensile tests or (2) they had occasion to perform tensile tests. Each subject worked with a sample one yard square cut from the same 60-yard length of cloth which had previously been marked off for cutting and testing, as shown in Figure 1.

Each piece was marked into quadrants, and each operator tested the quadrants marked *W* (for warp strength) and those marked *F* (for filling strength), lining up the fabric by eye in the jaws of the machine, as would normally be done on any other cloth under test at this Depot.

All samples were permitted to come to moisture equilibrium under standard textile-testing conditions.[5] One pendulum-type machine was used for all tests in the conditioned testing laboratory at the

[3] Under the direction of Captains B. Alford and H. Smith.

[4] Right twill 3/1; texture $116W \times 56F$; specification minimum strength $155W \times 105F$ (USAG-201B).

[5] 70°F, 65 percent relative humidity.

TABLE I. METHOD OF RATING "BREAKS" QUALITATIVELY

Code	Rating	Direction of tear	Relation of tear to jaws of machine
E	Excellent	Horizontal	Equidistant between jaws
G	Good	Horizontal	Closer to one of the jaws
F	Fair	Diagonal	Must not originate in the jaws
P	Poor	Not applicable	Tear originates in one of the jaws

TABLE III. CONTROL LIMITS[6] ON ORIGINAL AVERAGES AND RANGES

	Warp control limits			Filling control limits		
Limits for →	LCL	CL	UCL	LCL	CL	UCL
Averages chart	140.1	150.0	159.9	99.0	106.4	114.0
Range chart	0.0	17.2	36.3	0.0	12.9	27.4

[6] LCL = lower control limit, CL = center line, UCL = upper control limit.

TABLE IV. CONTROL LIMITS ON FIRST REFINEMENT OF DATA

	Warp control limits			Filling control limits		
Limits for →	LCL	CL	UCL	LCL	CL	UCL
Averages chart	139.6	149.5	159.4	98.9	105.8	112.7
Range chart	0.0	17.2	36.3	0.0	11.9	25.2

Depot. The machine was calibrated by the accepted dead-load method; jaw separation under no load was 12 ± 2 inches per minute; jaw dimensions were 1×1 inches, separated by 3 inches at the start of the test. No attempt was made to control or correct for belt slippage, ratchet friction, or pendulum inertia.

Each operator tested his fabric sample until ten acceptable (excellent, good, or fair) breaks had been obtained in the warp direction and ten in the filling direction, in accordance with the grab method outlined in Federal Specification CCC-T-191a. In all cases, dial readings in pounds and qualitative break evaluations were checked by a single experienced individual (Table I).

The ten acceptable breaks in warp and in filling for each operator were divided into groups of five and the average and the range of each group of five were determined (Table II, columns 1–9, page 270).

TABLE V. CONTROL LIMITS ON SECOND REFINEMENT OF DATA

	Warp control limits			Filling control limits		
Limits for →	LCL	CL	UCL	LCL	CL	UCL
Averages chart	139.6	149.4	159.3	99.1	105.8	112.6
Range chart	0.0	17.0	36.0	0.0	11.8	25.0

TABLE VI. RELATIVE CONTROL OF SUBJECTS

	Table III	Table IV	Table V
Subjects in control, number of	38	37	37
Subjects out of control, number of	12	1*	0*
Cumulative percentage out of control	24%	26%	26%

* Number of operators out of control, after operators out of control in Tables III and IV were deleted from Tables IV and V, respectively.

The averages and ranges in Table II were presented graphically (Figure 2) and tabulated according to *Manual Z-1.3* of the American Standards Association; control limits were computed separately for the groups of warp breaks and filling breaks.

Those subjects (Table II, column 10) one or more of whose test averages or ranges appeared out of control according to the values of Table III were eliminated from the computation and a second series of control limits (Table IV) were established, based on the first refinement of the data.

In the second refinement of data a further elimination of subjects (Table II, column 11) one or more of whose test averages or ranges fell outside the new control limits of Table IV provided the third set of limits listed in Table V.

Comparison of the data of columns 1 to 9, inclusive, of Table II with the control limits listed in Tables III, IV, and V is indicated in columns 10–12, inclusive, of Table II and is summarized in Table VI.

A total of 13 operators, or 26 percent of those tested, showed lack of control in breaking-strength tests. From the engineering aspects of fabric construction and machine operation, it seems reasonable to assume that the fabric was statistically homo-

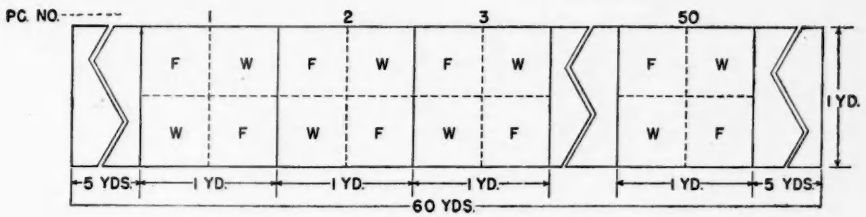

FIG. 1. *Method of laying out the 60-yard length of cloth for breaking-strength tests.*

TABLE II. AVERAGES AND RANGE OF WARP AND FILLING BREAKS OF THE FIFTY OPERATORS *

1	2	3	4	5	6	7	8	9	10	11	12
Operator's code number	Averages and ranges on warp strength tests (lbs.)				Averages and ranges on filling strength tests (lbs.)				Subjects out of control** on warp or filling averages or ranges according to limits of:		
	$Av._1$	$Av._2$	R_1	R_2	$Av._1$	$Av._2$	R_1	R_2	Table III	Table IV	Table V
1	147.6	156.2	14	22	(114.2)†	112.6	(26)	19	x	x	x
2	150.6	147.2	21	24	106.4	106.0	21	16			
3	147.4	150.8	20	23	107.8	105.2	13	17			
4	146.8	145.0	26	29	107.4	112.6	23	11			
5	151.8	152.8	11	32	105.2	102.6	(26)	9		x	x
6	150.0	(139.4)	23	28	(115.0)	110.0	16	12	x	x	x
7	149.8	156.8	27	23	103.6	104.4	15	6			
8	140.2	155.6	15	17	109.6	102.6	13	20			
9	155.8	146.6	20	10	108.2	112.0	12	17			
10	155.4	153.0	9	16	112.6	101.4	5	12			
11	141.2	150.0	35	25	103.2	111.6	15	10			
12	146.4	(136.6)	6	18	105.6	106.6	20	8	x	x	x
13	148.4	148.6	12	25	101.4	106.8	24	2			
14	154.8	152.4	24	15	(114.2)	108.2	23	22	x	x	x
15	144.8	152.6	15	17	109.8	106.4	10	8			
16	152.4	155.6	21	18	(114.4)	105.4	13	13	x	x	x
17	152.2	152.4	14	6	102.8	103.8	9	17			
18	147.0	155.8	10	16	101.8	109.6	19	9			
19	148.8	144.6	8	14	100.4	101.4	12	12			
20	148.0	148.2	17	26	106.8	106.0	16	10			
21	149.0	146.0	4	24	110.6	106.0	10	13			
22	140.8	143.4	27	32	99.8	100.2	10	8			
23	155.6	152.6	7	15	105.4	103.4	10	7			
24	147.4	148.0	26	14	105.0	110.2	15	6			
25	149.2	143.8	6	18	111.6	106.6	17	24			
26	151.2	151.4	6	15	111.4	101.2	(33)	10	x	x	x
27	155.6	(139.2)	18	11	105.8	101.0	16	11	x	x	x
28	142.4	143.2	30	32	105.2	105.2	8	15			
29	150.8	153.2	12	15	103.2	103.8	9	4			
30	158.6	(162.2)	9	7	111.0	109.6	19	21	x	x	x
31	148.4	(139.8)	20	20	101.0	105.6	13	13	x	x	x
32	143.0	150.2	33	24	102.2	100.0	5	5			
33	158.6	153.8	11	14	110.4	(116.6)	15	13	x	x	x
34	(163.0)	(159.4)	21	18	106.8	105.4	6	14	x	x	x
35	149.4	145.6	23	17	102.6	107.4	9	9			
36	156.0	155.4	13	10	110.6	111.6	8	7			
37	155.6	154.2	17	6	109.2	108.0	11	22			
38	153.4	157.0	8	15	110.4	109.8	8	5			
39	146.0	144.6	8	14	103.6	102.8	14	21			
40	148.2	147.8	20	10	106.8	103.8	19	13			
41	143.4	148.0	18	13	103.2	105.6	16	7			
42	152.0	153.6	11	13	107.4	106.8	20	6			
43	145.4	147.4	19	18	109.8	103.0	18	5			
44	147.2	144.4	17	11	103.4	99.6	13	11			
45	152.2	152.8	12	12	107.6	106.6	5	12			
46	146.6	154.8	10	17	103.2	107.0	7	9			
47	152.4	154.4	6	9	105.0	104.0	5	13			
48	150.4	150.6	(40)	14	103.4	106.8	13	20	x	x	x
49	152.6	149.4	14	24	104.8	106.2	9	13			
50	150.0	156.6	22	15	107.2	106.0	8	8			

* Source: Results of tests performed at the Philadelphia Quartermaster Depot.
† ( ) in body of table indicates the value which is out of control.
** x indicates operator out of control.

geneous and that the machine was statistically uniform in its operation. This leaves only the technique of the operator open to question with respect to the statistical uniformity of results. Therefore when the records show one or more points to be out of control, the technique of the operator is interpreted as erratic or faulty. This interpretation is further confirmed by the fact that all operators who were

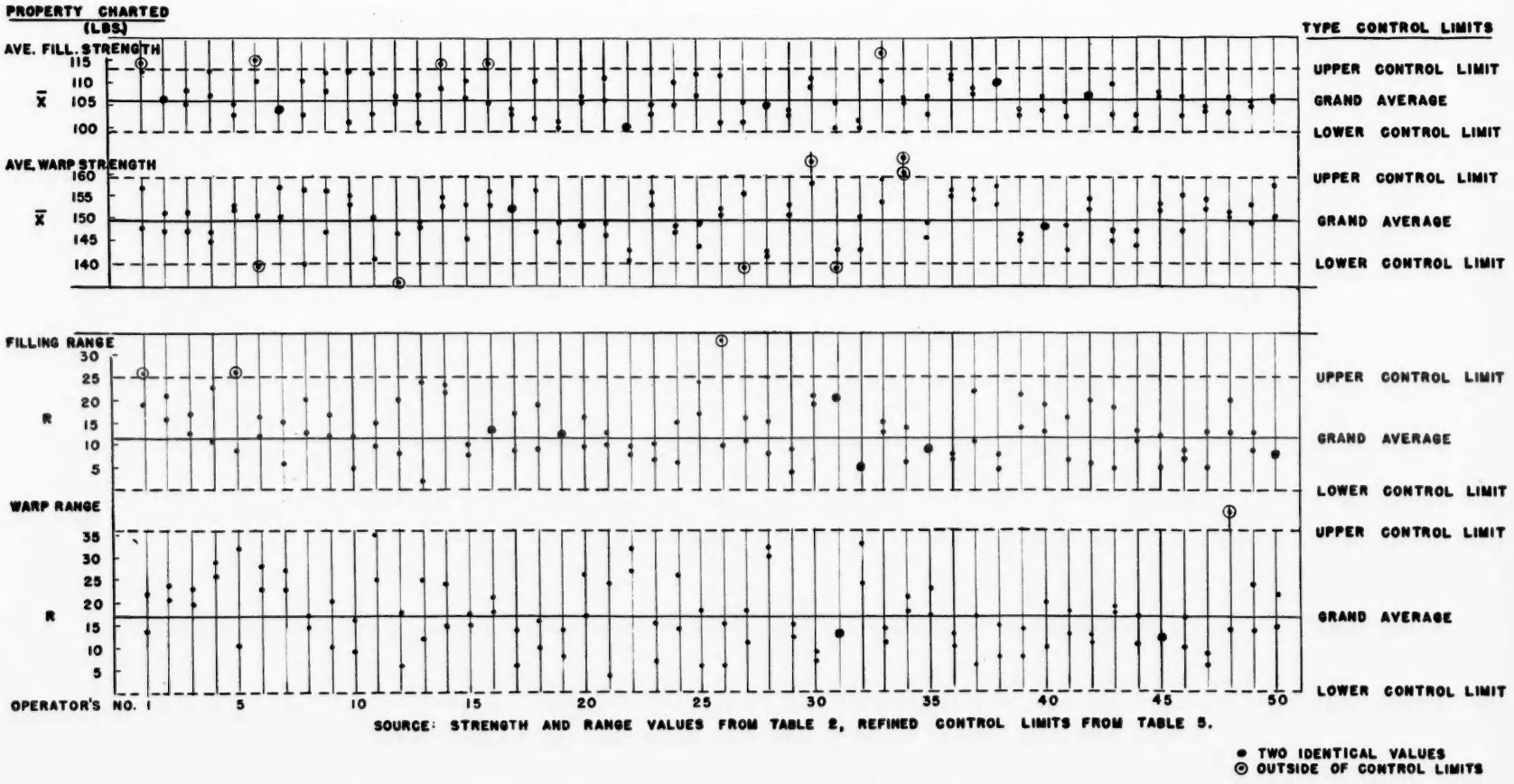

FIG. 2. *Chart of the statistical control of breaking-strength testing of cotton fabric obtained by a group of 50 laboratory workers at the Philadelphia Quartermaster Depot.*

TABLE VII. COMPARISON OF AVERAGE BREAKING STRENGTH OBTAINED BY JAW BREAKS VERSUS ACCEPTABLE [7] BREAKS

	Warp		Filling	
	Type of break		Type of break	
Item calculated [8]	Acceptable	Jaw	Acceptable	Jaw
Number of observations	370.0	160.0	369.0	186.0
Average breaking strength	149.4	137.3	105.8	102.2
Standard deviation of breaking strength	8.03	11.09	5.74	7.32
Coefficient of variation	5.4%	8.1%	5.4%	7.2%
Are differences between acceptable- and jaw-break averages significant?	Yes ($t=14$)[9]		Yes ($t=6.3$)	
How much lower is average strength of jaw break than that of acceptable break?	8.1%		3.4%	

[7] Acceptable breaks are those rated "F" or better in Table I, and jaw breaks are those rated "P" in Table I.

[8] Calculations are based on the individual observations of the refined data.

[9] Students' "t" test.

TABLE VIII. ASSOCIATION [10] BETWEEN TYPE OF BREAK AND CONTROL OF TESTING

	Warp contingency		Filling contingency	
Number of	For operators in control	For operators out of control	For operators in control	For operators out of control
Poor breaks	160	60	186	63
Fair breaks	236	84	313	116
Good breaks	86	30	47	11
Excellent breaks	48	16	9	3
Statistics [11]	$X^2 = 0.1733$		$X^2 = 1.7889$	
	$C = 0.0156$		$C = 0.0488$	

[10] The strength of association is given by the C values above.

[11] Where: X^2 = chi square; C = coefficient of mean-square contingency.

Interpretation of C values: These values of C could have been obtained from sampling or chance: on warp, 98 out of 100 trials; on filling, 70 out of 100 trials.

known to have a matured technique and who had performed these tests continually not only showed good control but actually obtained close averages and fairly close ranges within their averages. This is verified by the data in Table II for operators 9, 10, 20, 24, 36, 37, 38, 40, 42, 45, 46, 47, 49, and 50, who were in the experienced operators' class and were doing breaks routinely. In several cases experienced operators, notably 31 and 34, whose techniques were highly regarded, were out of control. These operators, however, did not meet the qualification of having performed the tests continually. Actually, they had performed tests at infrequent intervals. In one case, the operator (27) met both criteria except that it was well known that this person's testing was erratic and he was, therefore, not considered to have the mature technique specified for those in control. The other operators (1, 5, 6, 12, 14, 16, 26, 30, and 33) who were out of control were ones who had performed breaks at infrequent intervals.

The data were analyzed on the basis of jaw breaks versus acceptable breaks to establish the significance of the difference between average tensile strengths based on each type of break. The data listed in Table VII show evidence of jaw breaks occurring through cutting action brought about by excessive tightening of the jaws, as well as the results of uneven mounting accompanied by concentrated stresses in the fabric near the clamped portion.

Further examination of Table VII shows that jaw breaks are from 3 percent lower (filling) to 8 percent lower (warp) than acceptable breaks; these differences are highly significant. A further condemnation of jaw breaks is revealed by the fact that jaw breaks show much more variability (see "Coefficient of variation") than the acceptable breaks.

The concept that subjects with extensive experience in performing tensile-strength tests on fabrics are able, in addition to obtaining more consistent values, to produce fewer jaw breaks is not supported by the data. The answer to the question whether those in control obtain fewer jaw breaks than those out of control is negative. An examination of the number of jaw breaks reveals that there were 346 jaw breaks obtained for the 37 subjects in control as against 123 jaw breaks for the workers not in control. That is an average of 9.35 as against 9.46 per person for operators not in control. Analysis shows this difference to be insignificant. It was found that if jaw breaks were considered as defective breaks, then the percent of defective breaks based on the total number of breaks obtained by those out of control (31.6 percent) was not significantly greater than for those in control (30.2 percent). If the importance of mounting the specimen and tightening the jaws hold as criteria for jaw-break production, then the experience and training of the operator who produces statistically controlled testing are not reflected in the control of the criteria.

TABLE IX. COMPARISON OF AVERAGE STRENGTHS OBTAINED BY DIFFERENT TYPES OF BREAKS ON UNIFORM TWILL BY 37 OPERATORS[12]

Types of Breaks[13]	Symbol	Results on warp strength Defective, effective, or acceptable				Results on filling strength Defective, effective, or acceptable			
		P	*F*	*G*	*E*	*P*	*F*	*G*	*E*
Number of breaks	N	160.0	236.0	86.0	48.0	186.0	313.0	47.0	9.0
Average breaking strength (lbs.)	$\bar{X}$	137.3	148.2	152.3	150.5	102.2	105.7	106.1	109.1
Standard deviation	Sx	11.09	7.635	8.22	8.145	7.32	5.555	6.785	5.14
Standard error	$S_{\bar{x}}$	0.877	0.497	0.886	1.176	0.537	0.314	0.990	1.712
Coefficient of variation	$\frac{Sx}{\bar{x}}(100)$	8.1%	5.2%	5.4%	5.4%	7.2%	5.3%	6.4%	4.7%
Test for significant difference between average strengths obtained by each type of break[14]	Line 1	x...HS...x				x...HS...x			
	Line 2	x.....HS.....x				x.....HS.....x			
	Line 3	x.....HS.....x				x.....HS.....x			
	Line 4		x...HS...x				x...NS...x		
	Line 5		x.....NS.....x				x.....NS.....x		
	Line 6			x...NS...x				x...NS...x	

[12] These operators were shown to be in statistical control in breaking-strength tests.
[13] Poor, fair, good, excellent.
[14] HS—Highly significant difference exists between columns marked "x."
NS—No significant difference exists between columns marked "x."
x—This mark shows the columns compared.

Actually from observation it is known that a good operator practices uniformity in mounting his fabric in the machine but cannot easily control the pressure with which he tightens the jaws.

Similarly, breakdown of the data (Table VI) into types of breaks (poor, fair, good, and excellent) showed, by the "chi-squared" test, no significant relationship between the control of an operator and his proportion of the various types of qualitatively evaluated breaks. Thus there is no reason to believe from the data studied that the skill of the operator determines how good or bad his breaks will be (skill being defined as statistical control with relation to the entire group of subjects).

Examination of Table VIII shows that the number of fair breaks greatly exceeds the number of poor, good, and excellent breaks. It seems, therefore, that the F-type break is the natural method of failure on this fabric.

Carrying the analysis further, a comparison was made of the types of breaks and their respective breaking-strength values as cited in Table IX. This table shows the result of "t" tests between the columns marked "x" in the body of the table. Only values obtained by operators in control are used. The "t" tests were performed separately for warp and filling results. There is a marked difference between *P* (that is, jaw breaks) and *F*, *G*, and *E* breaks (types of acceptable breaks) for warp. Strangely enough, there is a marked difference between strength secured by *F* and *G* breaks (line 4) but no real difference between *F* and *E* (line 5). The difference between *G* and *E* (line 6) is likewise not significant. The filling breaks, compared on a like basis, show a progressively decreasing significance between *P* on one hand and *F*, *G*, and *E* on the other (lines 1, 2, and 3). No real difference between strength obtained by *F*, *G*, and *E* is noted (lines 4, 5, and 6).

Finally, analysis of the general concept that the average breaking strengths obtained by operators not in control would be lower than the values obtained by the more experienced subjects illustrated that in some instances less-experienced operators

were out of control on the high side. If we assume operators in control to be those having the skill needed to perform a breaking test, then it may be stated that a skillful operator will tend to get more consistent results, not higher averages, than his less skillful coworker.

Conclusions

1. What proportion of operators who perform breaking-strength tests, occasionally or continually, obtain reliable results and what are the criteria which make an operator eligible to perform such tests?

From the results obtained it may be stated that only those who perform breaking-strength tests continually, and who are rated as having a matured technique, showed statistical control in testing. This follows from the fact that of those participating in the test 26 percent were out of control and no individual in this 26 percent met the two criteria.

2. Does a good operator obtain fewer jaw breaks than a poor operator; does he obtain a better type of failure (rated as *P, F, G,* and *E*) than a poor operator?

The data indicate that the number of jaw breaks is not indicative of the operator's skill; nor is the type of break (*E, G,* or *F*) related to skill.

3. Does a good operator obtain higher average values in pounds for his breaks than a poor one?

No.

4. Are jaw breaks as satisfactory as acceptable breaks in rating the strength of a fabric?

Jaw breaks provided lower average values and higher variabilities than the acceptable breaks.

5. Do the average strengths obtained by the acceptable breaks (fair, good, and excellent) differ significantly among themselves?

No significant difference was noted.* Fair breaks occurred most frequently of all types noted in the investigation.

It is recognized that since the results obtained for operators in control were based on only one series of tests, no statement can be made as to whether those individuals in control would have remained in control if tested over a reasonable period of time. There is good reason to believe that many of them would have, especially those meeting the two criteria of matured technique and routine performance, inasmuch as results of these tests checked quite well with previous expectations regarding the skill of the operators.

It should be noted explicitly that the term "control" as used herein refers to an operator's results considered as a part of the results of a group of operators. Obviously, an operator can be controlling his own tests statistically and yet be out of control as regards the group.

Acknowledgment

The help of Miss Jane Kane in checking computations and of Captain Stanley Backer in his suggestions for presentation of this report is hereby gratefully acknowledged.

* Except for Table IX, line 4.

Convenient Adjustment to a Standard Velocity Gradient of the Fluidity of Anomalous Cuprammonium Solutions of Cellulose*

Carl M. Conrad and Verne W. Tripp

Southern Regional Research Laboratory,† New Orleans, Louisiana

Introduction

Although structural viscosity has been recognized for many years and has been intensively studied since about 1930, a satisfactory theoretical and experimental basis for dealing with the viscosity of linear high polymer solutions has not been found.‡ Of the great mass of data on the subject published in the literature, few can serve a permanent purpose because not all the conditions necessary for interpretation have been recorded. Yet by continued attack and by study of such findings as those of Peterlin [9], there is promise that the problem can eventually be solved. Until this is accomplished it would seem advantageous to control or record all those conditions which are known to affect the viscosity of solutions of high polymer substances.

In the case of linear high polymer solutions of sufficiently high molecular weight the rate of shear during measurement influences the magnitude of the observed viscosity. The rate of shear depends, in turn, on the pressure applied and, in the capillary viscometer with which we are principally concerned here, on the bore of the capillary. In 1941 a technique was described by Conrad [3] for reproducing, in viscometers of differing capillary bore and with varying hydrostatic head, the fluidity (or viscosity) of strongly anomalous cuprammonium solutions of cellulose. Instead of working at such low pressures that the rate of shear was negligible, or attempting extrapolation to such a low velocity gradient that Brownian motion would completely dominate and prevent orientation of the linear molecules during flow, fluidity readings were made at several different velocity gradients; and a line drawn through the points either passed through or was extrapolated to a common velocity gradient within the range of convenient observation. This technique was made practicable by the extensively confirmed observation that, within the usual range of gradients for fluidity measurements, a plot of the logarithm of the fluidity against the logarithm of the mean velocity gradient is a straight line within the limits of experimental error. Although Kroepelin [7] deduced a semilogarithmic relation for benzene solutions of caoutchouc, a re-examination of his data by statistical methods fails to show that the semilogarithmic relationship is any better than the double-logarithmic one. In cotton cellulose the semilogarithmic relationship was definitely inferior. In a viscometer with multiple volume discharge at successively decreasing head, the mean velocity gradient for each head interval can be determined by dividing the velocity gradient-time constant, based on Kroepelin's [7] formula, by the time of discharge. This constant can be determined once and for all as a part of the viscometer calibration.

Practical considerations and a general lack of knowledge of the degree of effects involved offer a considerable obstacle to the general acceptance of fluidity adjustments for velocity gradient. For one thing, measurements are commonly made in instruments of such a type that the degree of anomalous behavior is not revealed, *i.e.*, in Ostwald-type viscometers. Then, on the erroneous assumption that at sufficiently low velocity gradients (within the practical range of measurements) the anomalous effect disappears or is inconsequential, effort is directed toward securing measurements at as low a gradient as possible. That the effect does not disappear was early pointed out by Fikentscher [4] and more recently by Lyons [8]. Finally, the type of equip-

* Part of the subject matter of this paper was presented at the third meeting of The Fiber Society, at Clemson, S. C., April 14–15, 1944, under the title "The Determination of the Cuprammonium Fluidity of Slightly Degraded Cellulose."

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

‡ For a recent excellent summarization of the progress in this field see Philippoff [10].

ment and facilities available often would not permit ready adaptation, so that adjustment to a common velocity gradient could be made without considerable outlay or interruption of the work.

This paper, besides presenting data from a considerably larger variety of deteriorating causes than those given by Jelinek [6], describes a technique whereby, under certain conditions, velocity gradient adjustments, with reasonable accuracy, can be made with the single-discharge, or Ostwald-type, viscometer. In the present investigation, this technique was applied for the determination of the fluidity of "anomalous" cuprammonium solutions of cotton cellulose.

Experimental Procedure

The methods employed for the present measurements were for the most part described in a previous report [3]. Special attention was given to the construction of the capillaries. That the perfection of the bore is more important with anomalous solutions than with Newtonian solutions is readily evident from a consideration of the fact that the viscosity of an anomalous solution varies with the rate of shear, which, in turn, varies with the third power of the capillary bore employed. Capillaries may be imperfect owing to (1) ellipticity, or noncircular bore cross section, (2) to conicality, or nonuniform bore diameter, or (3) to any combination of these defects. By calibration with so-called "standard liquids," these defects are largely compensated for in Newtonian liquids by the calibration constants, but they cannot be compensated for in this way in non-Newtonian liquids where the viscosity is a function of the velocity gradient.

The capillaries were constructed commercially by shrinking glass tubing upon accurately prepared, cylindrical mandrels and were examined microscopically for any defects before acceptance for use. The ends of the capillaries were cut off perpendicular to the capillary axis, and the end intended for discharge was polished. The length of all capillaries was 5.00 ± 0.01 centimeters, measured with the aid of a measuring microscope. The bore diameters of the capillaries varied from 0.150 to 0.032 centimeter, determined by mercury calibration. The use of detachable capillaries with perpendicular ends, instead of capillaries permanently sealed to the burettes, made it possible to avoid error in diameter of bore caused by softening and contraction of the glass during attachment, as well as error in the kinetic energy correction from trumpet-shaped bore openings as discussed by Bingham and Thompson [2].

The cuprammonium generator used was similar to that [11] used at the Forest Products Laboratory, Madison, Wisconsin, and was constructed of copper. It gave cuprammonium solutions containing nitrite only to the extent of one-fourth of that found in solutions prepared in an all-glass generator during earlier studies [3]. The cuprammonium solution contained 30 ± 0.2 grams of copper and 165 ± 2 grams of ammonia per liter and was found to have a fluidity of about 77 rhes, varying slightly with batch. The nitrite content also varied slightly from 1.0 to 1.6 grams per liter. The density of the solution at 25°C was found to be 0.974 gram per cubic centimeter.

The apparatus used to dissolve the cellulose has not been described previously. A sketch of the essential features can be seen by reference to Figure 1. The burette (see Figure 1 of reference [3]), containing the cellulose sample, is attached by the stopcock, *H*, at its top to the combined vacuum and nitrogen service. Selection of either nitrogen or

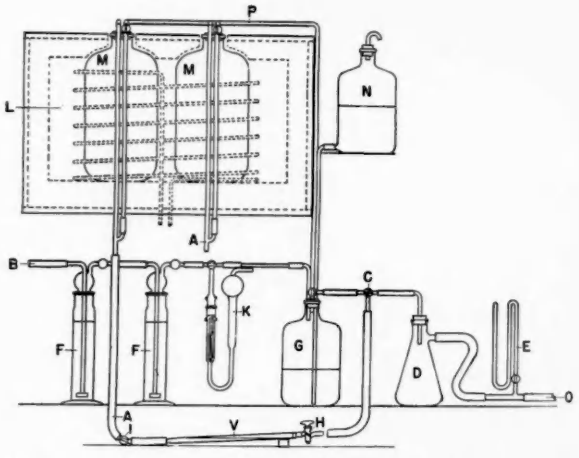

FIG. 1. *Apparatus for dissolving the cellulose in cuprammonium solution in the absence of oxygen. A—Cuprammonium supply line. B—Nitrogen supply line. C—Three-way stopcock, connecting vacuum line and nitrogen service with viscometer burette. D—Filter flask trap to vacuum line. E—Vacuum gauge. F—Gas washing bottles containing alkaline pyrogallol. G—Nitrogen capacity bottle. H—Stopcock at top of viscometer burette. I—Stopcock at end of cuprammonium supply line. K—Fog trap to test purity of nitrogen. L—Refrigerated storage chest, maintained at 10–12°C. M—Cuprammonium storage bottles surrounded by cooling coils. N—Pressure-head capacity bottle. O—Vacuum supply line. P—Nitrogen conducting tubes for replacement of cuprammonium solution as drawn. V—Burette viscometer.*

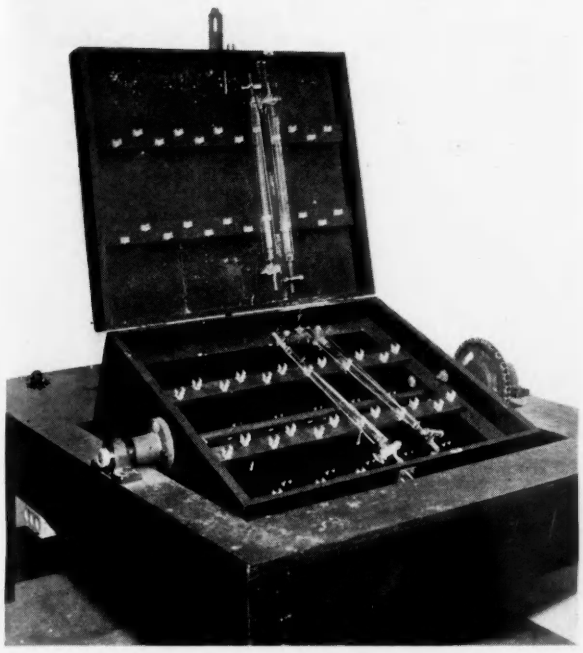

FIG. 2. *Rotating dispersion box with four burettes in place.*

vacuum is permitted by the three-way stopcock, *C*, which prevents both lines from being accidentally drawn on at the same time. A trap in the form of a 1-liter filter flask, *D*, is interposed in the vacuum line, and the degree of vacuum is indicated by the manometer, *E*. The nitrogen from a high-pressure cylinder is passed, with the aid of a constant pressure regulator with needle-valve control, through two scrubbers, *F*, containing alkaline pyrogallol, and thence into a 4-liter bottle, *G*. A pressure head, of about 3 feet of water saturated with sodium chloride, is maintained with the aid of an aspirator bottle, *N*, of the same size on a shelf above. The salt water, having only one-tenth the capacity for dissolved oxygen [4] as ordinary distilled water, greatly reduces the back diffusion of oxygen from the air into the capacity bottle during continued use. The head pressure on the nitrogen line also helps to avoid any diffusion of oxygen from the air into it due to possible leak or permeability of the rubber tubing. The purity of the nitrogen can be tested at any time as described by Zimmermann [12] by means of a phosphorus fog trap, *K*, located just beyond the second alkaline pyrogallol bottle, *F*. By means of a three-way stopcock, the stream of nitrogen may be made to pass from either direction through a tube containing yellow phosphorus sticks, thence through water, and finally through a larger bulb for observing any white cloud which would indicate the presence of oxygen. Zimmermann [12] states that as little as 0.0001 percent oxygen in the nitrogen can be detected by this means. Nitrogen from the capacity bottle, *G*, is also maintained over the cuprammonium reagent in the bottles, *M*, located in the refrigerated storage chest, *L*, above.

With the burette containing the sample lying flat on the table and attached to the nitrogen supply from *G* by means of the stopcock, *H*, at its upper end, and with the lower end open, *H* is opened, and the stopcock, *C*, turned to release nitrogen through the burette and thus sweep out the major portion of the air. When about three volumes of nitrogen have passed through the burette, the lower end, on which is a short length of rubber tubing, is attached to the cuprammonium supply line, *A*, the stopcock, *I*, being closed. Stopcock *H* still being open, stopcock *C*, after being turned to connect the vacuum line, is opened cautiously to avoid displacing the sample in the burette, until the pressure within the burette is equalized with that in the vacuum trap, *D*. Stopcock *C* is now carefully turned to refill the burette with nitrogen from bottle *G*. Evacuation and refilling of the burette with nitrogen is repeated twice more, after which stopcocks *C* and *H* are closed. The burette is now disconnected from the nitrogen-vacuum line and the stopcock end raised about 3 inches from the table. Stopcocks *I* and *H*, in the order named, are now opened, and the burette is filled about two-thirds of the way with cuprammonium reagent. Stopcocks *H* and *I* are closed, and the burette is given an energetic shaking, without being disconnected, to wet thoroughly and disperse the sample. Finally, the burette is held vertically and is filled up to the point where the cuprammonium reagent appears in the capillary at the top of the rubber stopper, but where it has not yet passed through stopcock *H*. Stopcock *I* is partly withdrawn, so that the rubber tubing on the burette can be closed with a pinch clamp, after which it is separated completely. The small amount of cuprammonium reagent which remains in the rubber tubing is rinsed out with water. Rubber bands are attached to the stirrups at the top and bottom of the burette to keep the stopcock assembly securely seated, and the burette, thus assembled, is placed in a rotating box (Figure 2). The box is allowed to rotate end-over-end at approximately 2 r.p.m. for 10–15 hours, conveniently overnight. The burettes are then taken

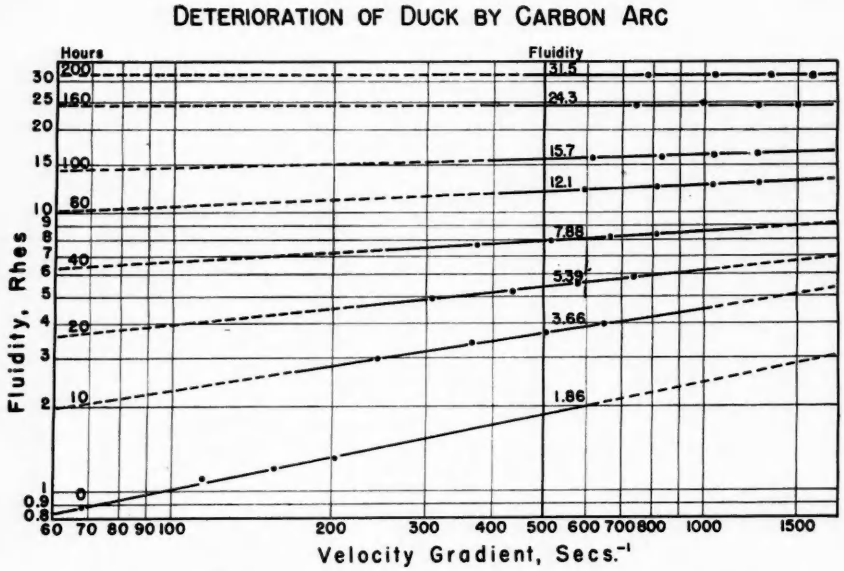

FIG. 3. *Curves showing relation of fluidity to velocity gradient for cuprammonium solutions of cotton duck, deteriorated by exposure for different periods of time to the carbon arc of a weather-testing unit. Figures at the left near ordinate axis indicate hours of exposure; those near center above curves, the fluidity at 500 reciprocal seconds.*

from the rotating box; the rubber bands and stirrups are removed; and calibrated capillaries of suitable capillary diameter are inserted in the rubber tubing at the bottom of the burettes. The burettes are set in their glass jackets in an aquarium water bath until temperature equilibrium at $25 \pm 0.10°C$ has been established. The stopcocks at the top are opened, and the time of discharge for each volume interval is measured with a double-action stop watch.

The data are treated as previously described [3].

Results

Deterioration by Different Agents

The influence of exposure of unbleached cotton duck to the unfiltered carbon arc in a weather-testing unit for various time periods, up to 200 hours, on the fluidity of the cellulose is shown by the series of curves in Figure 3. In agreement with the findings of Jelinek [6] on samples of cotton goods deteriorated by household wear and laundering, it was found that increasing lengths of exposure to the carbon arc led to increasingly higher curves with progressively smaller slope. At 25 rhes the fluidity-velocity gradient curve was almost, if not actually, parallel to the abscissal axis. The linearity of the curves on double-logarithmic plot is evident in Figure 3.

The influence of exposure to outside weathering on the fluidity of the cellulose of unbleached osnaburg is shown in Figure 4. It is evident that the first month of exposure caused a greater increase in fluidity than any subsequent period of equal length. Again the logarithmic slope decreased as the fluidity increased.

Figures 5 and 6 show the effects on the measured fluidities of heating cotton tire cord in contact with air.

Figure 5 shows the influence of different temperatures up to 160°C maintained for 17 hours on the fluidity of cotton cellulose. It is evident from the figures that de-

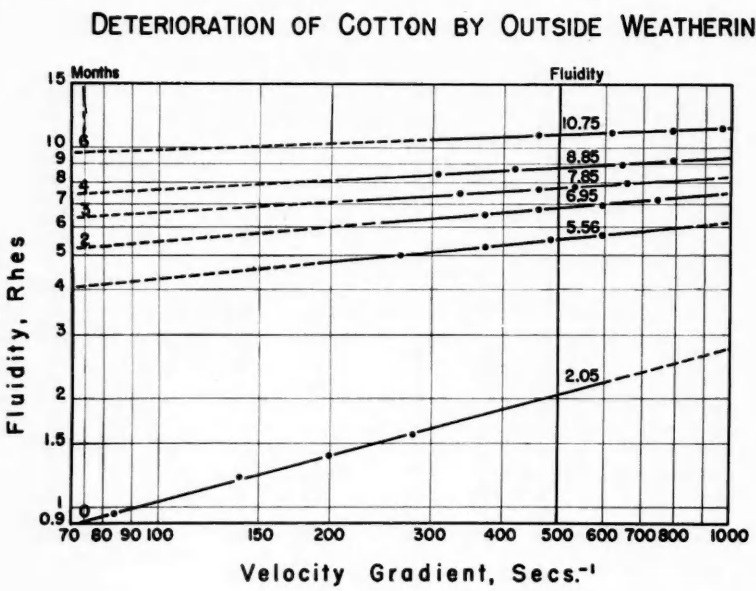

FIG. 4. *Curves showing relation of fluidity to velocity gradient for cuprammonium solutions of unbleached cotton osnaburg, exposed to outdoor weathering for different periods. Figures at left near ordinate axis indicate months of exposure; those near center above curves, the fluidity at 500 reciprocal seconds.*

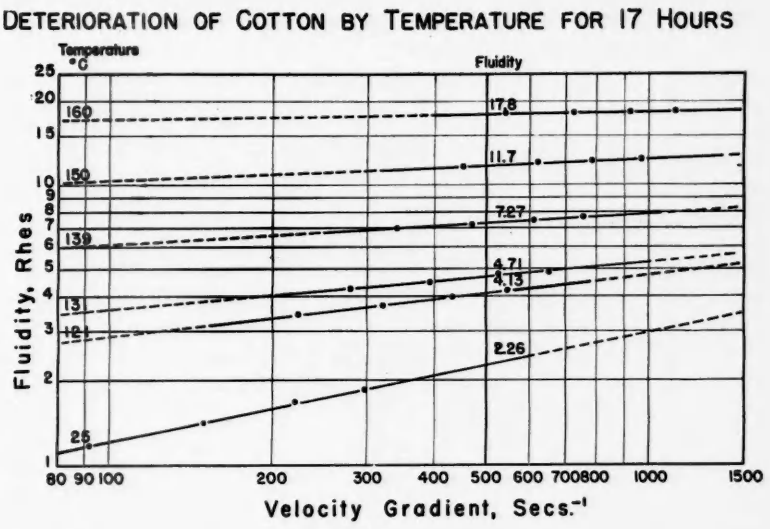

FIG. 5. *Curves showing relation of fluidity to velocity gradient for cuprammonium solutions of cellulose from cotton tire cord, heated in air at various temperatures for 17 hours. Figures at left near ordinate axis indicate temperatures of exposure; those near center above curves, the fluidity at 500 reciprocal seconds.*

terioration was more rapid as the temperature was increased. Figure 6 shows that prolonged exposure over a number of days at temperatures as low as 125°C causes very extensive deterioration.

In Figure 7 is shown the effect of period of heating in a special boiling treatment, with 2–3 percent sodium hydroxide, on the fluidity of the cellulose of cheesecloth. The slope of the logarithmic curves relating fluidity and velocity gradient decreased progressively as the fluidity increased.

In Figure 8 are shown the progressive increase in fluidity of partially acetylated cellulose and the progressive decrease in the logarithmic slope of the fluidity-velocity gradient curves as the degree of acetylation increases. The acetylation was brought about through catalytic action of perchloric acid. In this case, allowance had to be made in concentration adjustments for the weight of the acetyl groups which are removed by saponification by the cuprammonium reagent used for the dissolution.

Relation of Logarithmic Slope to Fluidity

It is evident from the results shown in Figures 4–8, where the differences in the curves may be regarded as associated with molecular degradation of the solute and not with a physical condition of the solution, that increasing fluidities are associated with decreasing logarithmic slopes. It is likewise evident that, if the relationship is sufficiently exact and not too complicated, a means might be established for conveniently adjusting the fluidity values of cuprammonium solutions of cellulose that show anomalous behavior to a given velocity gradient, even with use of single-discharge viscometers, of the Ostwald type, and without the necessity of applying varying external pressures.

Data from some 451 samples—giving in concentration of 0.5 gram per 100 milliliters a range of fluidities from 1.48 to 60.3 rhes and more or less deteriorated by such methods as outdoor weathering,

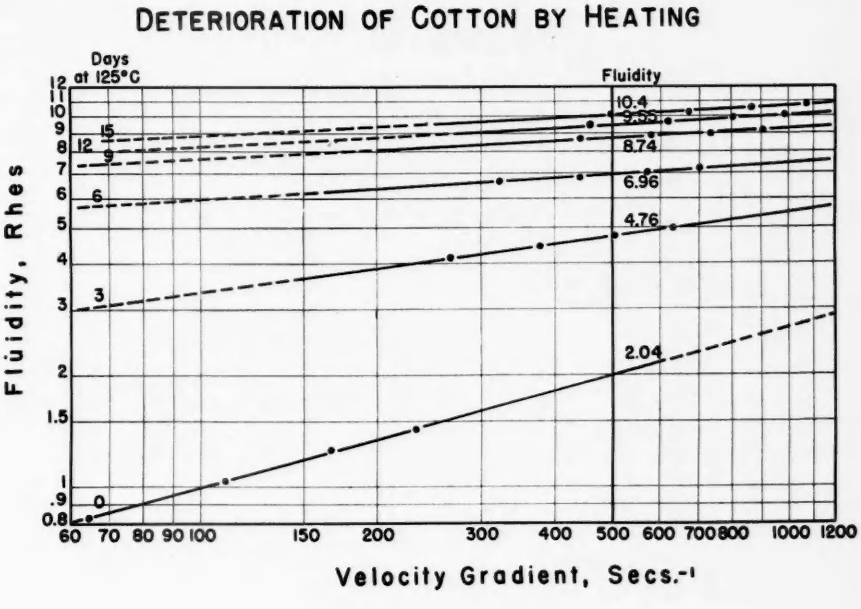

FIG. 6. *Curves showing relation of fluidity to velocity gradient for cuprammonium solutions of cellulose from cotton tire cord heated at 125°C for different periods. Figures at left near ordinate axis indicate number of days of exposure; those near center above curves, the fluidity at 500 reciprocal seconds.*

exposure to ultraviolet radiation of the mercury or carbon arc, acid hydrolysis, heating, kier boiling, and partial acetylation—were used to find the relation between logarithmic slope and fluidity. Since the logarithm of the fluidity gives a straight line with the logarithm of the velocity gradient, the slope, S, of this line can be determined by the usual formula.

$$S = \frac{\log F_1 - \log F_2}{\log G_1 - \log G_2} = \frac{\log F_0 - \log F_{500}}{\log G_0 - \log G_{500}} \quad (1)$$

where F and G refer to fluidity and velocity gradient, respectively, and the subscripts 1, 2, 0, and 500 refer to observed values and the values at a velocity gradient of 500 reciprocal seconds, respectively. All the values on the right of the first equality sign are taken or interpolated from the viscometer observations.

When the logarithmic slopes determined in this way were plotted against the logarithms of the corresponding fluidities, read off at a velocity gradient of 500 reciprocal seconds, a curve slightly concave upward was indicated. Various types of curves were fitted to the observations. While a logarithmic polynomial gave the most perfect fit, the resulting equation would not yield an expression solvable for the fluidity at 500 reciprocal seconds in terms of the observed fluidity and velocity gradient. Finally, a curve represented by the equation

$$S = 0.325 (\log F_{500} - 1.5)^2 \quad (2)$$

was found to give a very satisfactory representation of the data as shown in Figure 9. This curve is a parabola, tangent to the log F_{500}-axis with the vertex at log $F_{500} = 1.5$ (*i.e.*, $F_{500} = 31.6$ rhes). While mathematically the curve turns up beyond log $F_{500} = 1.5$, cuprammonium solutions containing 0.5 gram of cellulose per 100 milliliters with fluidities above this limit may be considered to be essentially Newtonian in their behavior, and thus that portion of the curve may be ignored.

Combining equations (1) and (2), substituting 2.7 for log G, the equivalent of log 500, and transposing, there is obtained

$$\log F_0 = \log F_{500} + 0.325 (\log G_0 - 2.7)(\log F_{500} - 1.5)^2 \quad (3)$$

and solving for log F_{500},

$$\log F_{500} = A \pm \sqrt{A^2 - 2.25 + \frac{3.077 \log F_0}{\log G_0 - 2.7}}, \quad (4)$$

where

$$A = 1.5 - \frac{1.538}{\log G_0 - 2.7}. \quad (5)$$

The minus sign is to be used in equation (4) when the observed mean velocity gradient is below 500 reciprocal seconds; the plus sign, when it is above 500 reciprocal seconds.

From the residuals of the observations about the curve of Figure 9 the standard error of estimate was computed. This amounted to $\Delta S = 0.0185$.

After equation (2) had been fitted to the pooled data from different types of degradation, it was tested by plotting the data separately and noting whether the observations scattered uniformly about the curve or tended to segregate above or below it. It was thus determined that degradation by irradiation in the weather-testing unit, by exposure to the mercury arc, by progressive partial acetylation, by outdoor weathering, or by heat, did

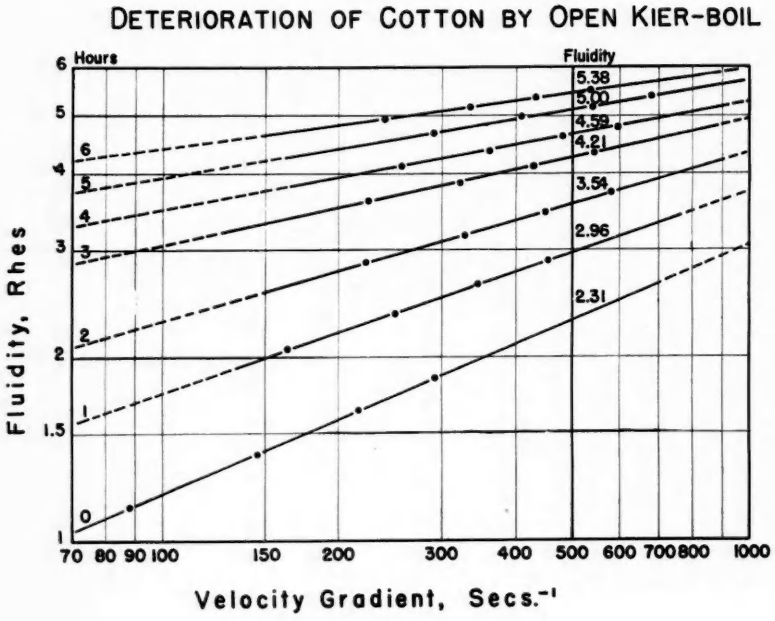

FIG. 7. *Curves showing relation of fluidity to velocity gradient for cuprammonium solutions of the cellulose of cheesecloth, heated in the open kier with 2–3 percent caustic for different periods. Figures at left near ordinate axis indicate number of hours of heating; those near center above curves, the fluidity at 500 reciprocal seconds.*

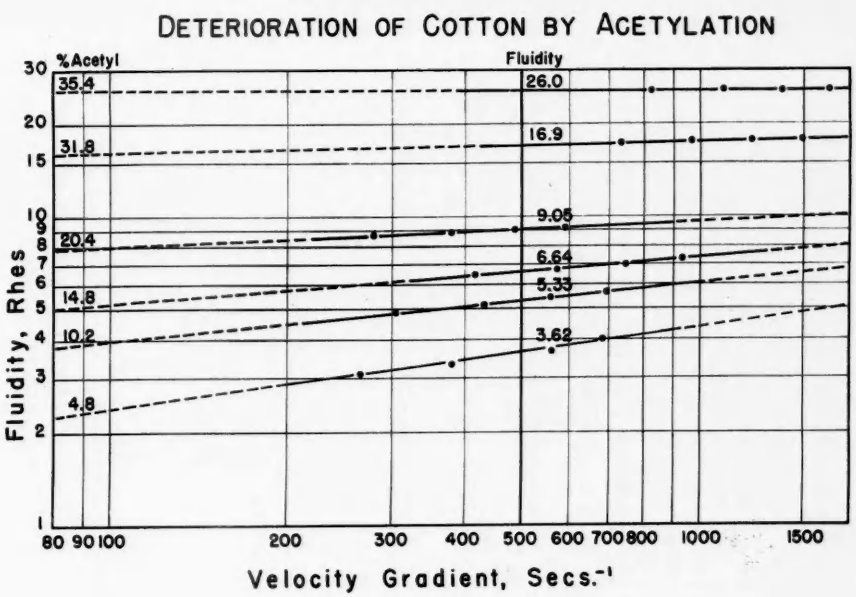

FIG. 8. *Curves showing relation of fluidity to velocity gradient for cuprammonium solutions of cellulose regenerated from cellulose acetate of varying acetyl content. Figures at left near ordinate axis indicate acetyl content of cellulose; those near center above curves, the fluidity at 500 reciprocal seconds.*

not give rise to a noticeably different scatter about the curve of equation (2).

If the fluidity is determined at or adjusted to a concentration of 0.50 gram cellulose per 100 milliliters of cuprammonium solution, equation (4) permits calculation of the fluidity at a velocity gradient of 500 reciprocal seconds from a single efflux volume, measured at some other mean velocity gradient. Small variations of concentration, say between 0.45 and 0.55 gram per 100 milliliters, have relatively minor effect on the slope of the fluidity-gradient line and permit adjustment of fluidity for concentration, but large variations such as are frequently used in extrapolation to zero concentration may have a very significant effect on the slope, depending on the molecular degradation of the particular sample. The equation has not been tested for cuprammonium solutions other than those complying with the American Chemical Society [1] specification, and the use of some other composition would require verification and probably some change in the constants of the equation.

Precision of Estimating Fluidity at 500 Reciprocal Seconds

From the standard error of estimate, $\pm$ 0.0185, of S, the resulting error in the fluidity at 500 reciprocal seconds may be computed. Solving equation (1) for log F_{500} and taking partial differentials with respect to S:

$$\partial \log F_{500} = -(\log G_0 - 2.7)\partial S.$$

But

$$\partial \log F_{500} = 0.4343 \frac{\partial F_{500}}{F_{500}}.$$

Therefore

$$0.4343 \frac{\partial F_{500}}{F_{500}} = -(\log G_0 - 2.7)\partial S$$

and

$$\frac{\Delta F_{500}}{F_{500}} = -2.3(\log G_0 - 2.7)\Delta S.$$

But

$$\Delta S = \pm 0.0185.$$

Therefore, since the minus sign preceding 2.3 is immaterial,

$$\pm \frac{\Delta F_{500}}{F_{500}} = \pm 0.0426(\log G_0 - 2.7).$$

It is thus shown that the ultimate error in the adjusted fluidity depends not only on the error made originally in estimating S but also on the range, log $G_0 - 2.7$, through which the adjustment must be made. When G_0 is between 100 and 500 reciprocal

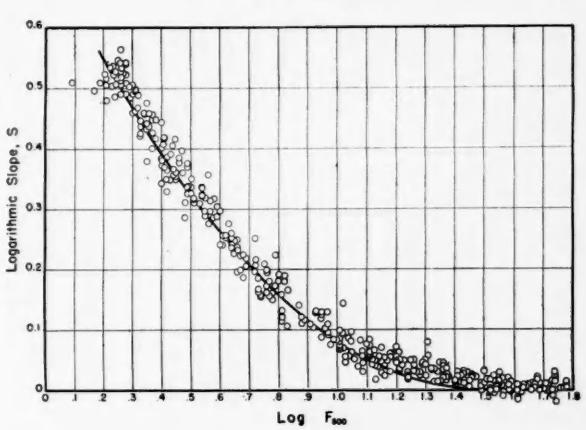

FIG. 9. *Curve showing the relationship between the slope of logarithmic fluidity-velocity gradient curves and the logarithm of the fluidity at 500 reciprocal seconds.*

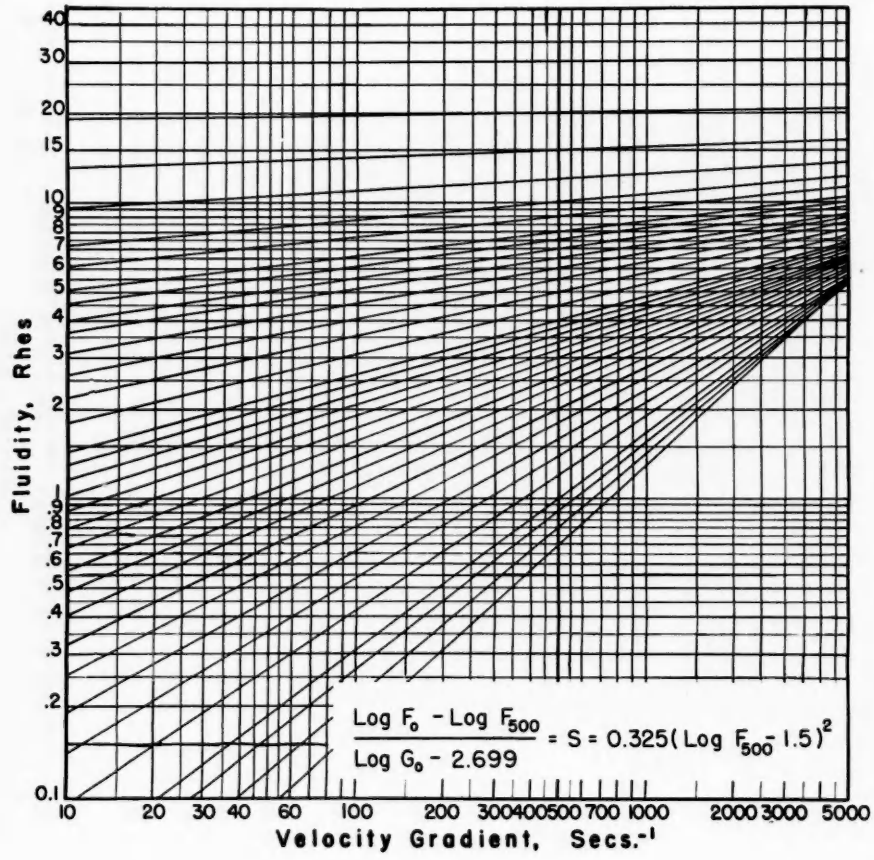

FIG. 10. *Fluidity,* F, *as a function of mean velocity gradient,* G, *for various selected values of the parameter,* F_{500}. *Each line on the graph corresponds to a different equation derived from equation (3) by substitution in it of a convenient value of log* G_0 *and different values of log* F_{500}.

seconds ($2.0 < \log G_0 < 2.7$), the maximum error in F_{500}, due to adjustment by equation (4), will be 1.3 percent. On the other hand, if the value of G_0 is between 500 and 1,000 reciprocal seconds ($2.7 < \log G_0 < 3.0$), the maximum error in F_{500} due to adjustment will not exceed 0.6 percent. These errors, of course, are associated entirely with the adjustment process and are exclusive of errors of observation of time of discharge, concentrations of solute, etc., attendant on the fluidity measurements.

Practical Application of the Adjustment

As it stands equation (4) is too clumsy for convenient everyday use. For routine purposes a chart, such as that shown in Figure 10,[4] is constructed with the aid of this equation. In this figure fluidity is plotted as ordinate against velocity gradient as abscissa. The oblique lines cutting across these coordinates represent the slope of fluidity with velocity gradient for cuprammonium solutions of cellulose which, at a velocity gradient of 500 reciprocal seconds, have the fluidity indicated by their point of intersection with this gradient.

In using Figure 10 for adjustment of fluidities, measured at other gradients, to the corresponding fluidities at 500 reciprocal seconds, it is first necessary to know the mean velocity gradient at which the observed fluidity was measured. This is readily computed from the instrumental velocity gradient constant K_G, where

$$K_G = \frac{8V}{3\pi r^3} = Gt, \qquad (6)$$

by dividing this by the measured time, t, of efflux. In equation (6) V is volume of the viscometer bulb, r is the capillary radius, in centimeters, and G is the mean velocity gradient during discharge. It is at once evident that the constant K_G is readily determined once and for all at the time the viscometer is being calibrated, with little, if any, extra work. By locating the observed fluidity and velocity gradient on Figure 10 and then interpolating parallel to the oblique lines to a velocity gradient of 500 reciprocal seconds, it is possible to make the adjustment of fluidity with negligible loss of time and with a satisfactory degree of accuracy for most practical applications.

Figure 10 shows the relatively large change in fluidity with velocity gradient that exists in the vicinity of one rhe and the relatively small effect that exists above 10 rhes. It is evident that the straight

[4] A few copies of this chart, drawn on logarithmic coordinates to a scale of approximately 14 by 16 inches, are available on request to the authors.

lines representing change of fluidity with velocity gradient must intersect at some gradient above 5,000 reciprocal seconds, but for practical purposes this is immaterial, since few, if any, fluidity measurements are ever made at such high gradients. In addition, it is found that the curves do not intersect at a common point but at successively larger gradients as the fluidity at 500 reciprocal seconds becomes larger.

Summary

Certain equipment and techniques for the determination of the fluidity of anomalous cuprammonium solutions of cellulose are described.

Curves are presented which show the logarithm of the observed fluidity as a linear function of the logarithm of mean velocity gradient of flow of cuprammonium solutions containing 0.5 gram per 100 milliliters of celluloses, degraded by the carbon arc, outdoor weathering, heat, kier boiling, or partial acetylation.

It is shown that at the low fluidities of undegraded celluloses the logarithmic slopes relating fluidity and velocity gradient are very steep and that, as the fluidity at any particular mean velocity gradient increases with progressive degradation, the slopes decrease until at a little over 30 rhes the anomalous behavior disappears.

An equation has been derived which relates the logarithmic slope of the fluidity-velocity gradient curve for cuprammonium solutions of cellulose containing 0.5 gram per 100 milliliters to the fluidity at 500 reciprocal seconds. This equation can be combined with a second equation to give the fluidity of cuprammonium solutions containing the same concentration of cellulose at a gradient of 500 reciprocal seconds from a single pair of fluidity and velocity-gradient values at any other gradient within the practical range of measurement. If cuprammonium reagent of the composition specified by the American Chemical Society is used, this equation permits a convenient adjustment of fluidity to a standard velocity gradient even though a single-discharge viscometer, such as the Ostwald, is employed.

A chart is suggested for the convenient approximate adjustment of fluidities to a common velocity gradient of 500 reciprocal seconds.

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Discussion of Published Papers

Supplementary Data for "The Mechanical Properties of Textiles, III"

Sidney Katz, George Halsey, and Henry Eyring

We are publishing this communication which presents supplementary data from the authors and Mr. Katz in connection with Part III of the series "The Mechanical Properties of Textiles." This paper appeared on page 13 of the January, 1946, issue of TEXTILE RESEARCH JOURNAL.

H. R. Bellinson * conducted a number of stress-strain experiments at various rates of loading on viscose yarn, 150/42, manufactured by the North American Rayon Corporation. They are here ana-

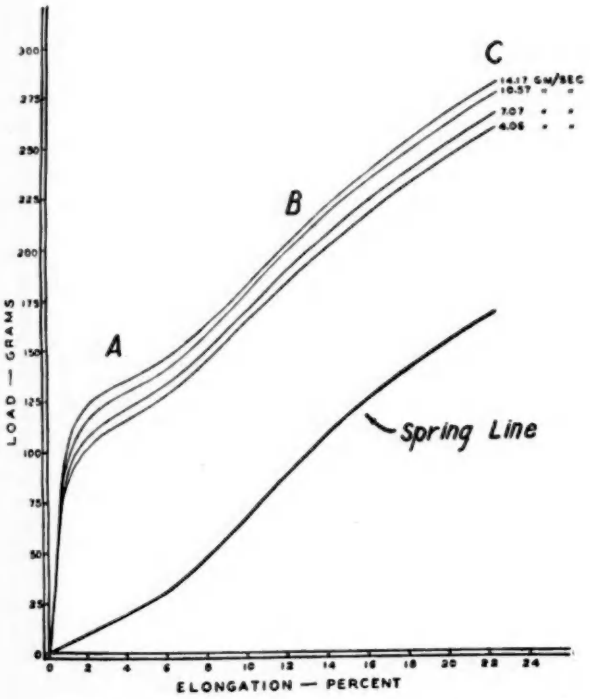

FIG. 13. *Bellinson's experiments.*

* Bellinson, H. R., TEXTILE RESEARCH **10**, 316 (June 1940).

TABLE I. DISTANCES MEASURED AT THREE INTERSECTIONS

Curve	Intersection		
	A	*B*	*C*
4	135.1	135.1	136.3
3	129.4	130.0	129.9
2	120.0	118.0	118.0
1	113.0	109.0	109.0

(Numbering of curves—1, bottom; ···4, top. Distances measured from curve drawn in (from curve 3) and extrapolated to origin.)

TABLE II. VALUES OF β CALCULATED AT THREE INTERSECTIONS

	A	*B*	*C*
β_1^2	3,850	413	413
β_2^4	71.8	60	25.4
β_1^3	365	72	73.5
β_1^4	297	92	73

(β_1^2—calculated from curves 1 and 2, etc., and referred to the bottom curve.)

TABLE III. DISTANCES CALCULATED USING $\beta = 500$

	Intersection					
	A		*B*		*C*	
	Rc	*Rm*	*Rc*	*Rm*	*Rc*	*Rm*
${}_1^2R$	1.08	1.06	1.08	1.08	1.08	1.08
${}_2^4R$	1.10	1.12	1.10	1.04	1.10	1.15
${}_1^3R$	1.14	1.15	1.14	1.19	1.14	1.18
${}_1^4R$	1.18	1.20	1.18	1.24	1.18	1.25

(R_c = R calculated; R_m = R measured.)

lyzed on the basis of the three-element non-Newtonian model. Figure 13 presents Bellinson's data, with the addition of a proper spring line.

Then, distances representing f_∞ were measured at positions A, B, and C, and β calculated with the formula

$$\beta = \tfrac{1}{2} n^{\frac{1}{R-1}}.$$

(This formula was printed incorrectly in Paper III proper.)

The results of this computation are presented in Tables I and II.

The fact that β varies from 25 to 3,850 seems to indicate that the theory fails completely to account for the experiment. However, this is because β is extremely sensitive and varies exponentially with the experimental data. Taking the value 500, to make the outside curves fit, the calculated positions of the other curves are in excellent agreement with the experiment (Table III). The error is well within the experimental error of this type of experiment.

Book Reviews

Postwar Prospects for American Textiles. Archibald M. McIsaac, James G. Smith, and John W. Cadman, Jr. Washington, Textile Foundation, 1946. 30 pages. Price, $1.00.

(Reviewed by S. J. Kennedy)

Once in a blue moon things happen that enable everyone to get off to a fresh start. Such is the situation now at the close of the war. The cutting off of normal replacement of equipment, the great accumulation of consumer buying power resulting from inflationary Government expenditures, and the chance to do a lot of thinking and planning before acting has presented such an opportunity to American Industry.

If we could see what the textile industry will look like five years from now, it would be much easier to make wise decisions about capital investment in some branch of the industry, buying or building a mill in that branch of the industry, deciding where to locate, or planning for expansion into new markets. Economics has been a hard teacher to the textile industries. Even those who have progressed well beyond the first-depression reader need occasionally to take a broad look at economic principles as they affect the future of textiles.

This is what the authors of *Postwar Prospects for American Textiles* have endeavored to do as they sketched out some of the industry's major areas of economic decision. This report represents an attempt to look at industry's problems as a whole. Most executives in the textile industry are very conscious of economic problems—in fact, in many respects textile markets and prices are almost classical examples of the kind of prices the economists have theorized about since the days of Adam Smith. They are markets in which prices respond to supply and demand so fluidly that practically everyone in the industry is a price economist of a sort.

However, knowledge of prices in the interaction of supply and demand for a given commodity does not qualify one to face longer-range economic problems. In fact, our industry has been much too much engrossed in the short-term economics of market prices to study adequately the longer-term implications of day-to-day occurrences. One has only to look at the history of the cotton textile industry over the past 25 years to realize how few firms have done any real long-range planning—in technological research, in orientation to markets, and in low-wage and low-purchasing-power policies.

It is not to be expected that a study of this kind covered by this report will be replete with newly discovered truths. Many of the facts of economics that need most to be emphasized are old truths which frequently have become so familiar as to have fallen into contempt. A restatement of broad perspective, particularly on the nature of the problem, is frequently needed, however, and it is especially needed at the present time.

At least four of the topics discussed in this report depend on markets, market analysis, and market demand: The section on "Postwar Demand for Textiles", is a summary of the important factors which may be expected to influence consumer taking of textiles. The section on "International Competition in Textiles" relates to the possibilities in markets abroad and aspects of foreign competition. The section on "Raw Materials" discusses the interrelation of supply and price positions of the different textile fibers. The section on "Modernization of Plant" concerns the basic question of what kind of product a mill should make, whether for a given market or some other one. It is pointed out that if the men in the industry are progressive in employing new machinery and methods, the industry's products will have a better chance of competing successfully with substitutes for textile products in the domestic markets than will older and inferior types of textile products.

In one sense it can probably be said that the most important decision with respect to postwar prospects is that of new capital investments, one that has already been made in most cases. Most mills have already decided what kind of equipment they will install in their plants and what kind of product they will make. All undoubtedly are trying to expedite their modernization program to get off to a fresh start, if possible, sooner than their competitors. It is to be hoped that they have planned not for the immediate postwar years but for the years after the industry's big modernization and re-equipment job is

completed. As the authors state, "with an intensified and increasingly fluid competition facing textiles, no manufacturer can afford to take his markets for granted. . . profits will depend in large measure upon the success with which research is utilized in anticipating the trends of consumer and industrial demands in producing textiles that meet those demands more effectively and at lower relative costs than rival commodities."

This approach to the study of markets is pointed up by the authors in their review of industrial organization. The emphasis which the inevitable though long-delayed trend toward aggregation of the industry into larger units has received during the war represents a drastic reappraisal of markets and marketing structures. The increased responsibility which the large industrial units will have to carry will call for statesmanship in economic matters.

It is to be hoped that broad industrial economic studies such as have characterized most American industries having large aggregates of management, and of which this report can be assumed to be a forerunner, will come to be a periodical occurrence in the textile industries and that textile economic thinking will increasingly come to transcend the day-to-day events of the market place.

Advancing Fronts in Chemistry, Vol. I. High Polymers. Edited by Sumner B. Twiss. New York, Reinhold Publishing Company, 1945. 196 pages. Price, $4.00.

(*Reviewed by L. W. Rainard*)

This book is a collection of lectures which were given at Wayne University by a series of well-known contributors in the field of high polymers. The book deals with varied aspects of polymer chemistry and physics, many of which are too complex for the brief treatment received in this book. While it can hardly be said that the book is detailed enough to be a good reference text, nor general enough to be a good classroom text, some of the subjects and treatments offered are of distinct value to those working in the field.

For the most part, the chapters are short reviews of the author's work or the specific field of the author's interest. Of especial value is the excellent chapter by Stockmayer on the work of Flory and Stockmayer on molecular size distribution and on branched and cross-linked polymers. A carefully presented and well-illustrated chapter by W. O. Baker on the nature of the solid state of chain polymers is included. Two able chapters on the mechanism of polymerization, one by C. C. Price and the other by F. R. Mayo, add considerably to the book. The chapter by Emil Ott on "The Effect of Chain Length on Physical Properties of Cellulose Derivatives" is very well done. In general, most of the remaining chapters are adequately handled, although there is some question as to whether the chapter by E. C. Pitzer on "Catalysis of Hydrocarbon Reactions" should be included in a work of this type.

It is rather difficult to produce an integrated volume when the chapters are written by numerous authors, each working independently; however, the material contained is valuable and the book should, at least, be read by workers in polymer chemistry.

Surface Active Agents. Theoretical Aspects and Applications. C. B. F. Young and K. N. Coons. Brooklyn, N. Y., Chemical Publishing Co., 1945. 381 pages. Price, $6.00.

(*Reviewed by Earl K. Fischer*)

In the past decade chemists in industrial laboratories have had at their disposal a variety of specialty reagents offered for an endless number of uses. Generically classified as surface-active agents, the utility of these compounds has been described in manufacturers' publications, patents, and trade journals. The task of writing a volume which is intended to assemble this information is indeed formidable.

One part of this book (153 pages) is devoted to a discussion of surface-tension measurements, the chemistry of typical compounds, and a listing of commercial products. The second part (204 pages) offers a variety of information on applications of surface-active agents in: emulsions, metal-cleaning, cosmetics, leather-processing, ore-flotation, inks, textiles, adhesives, foods, and lubrication. The list of commercially available compounds occupies 38 pages and appears quite complete. Illustrative recipes for various compositions are scattered throughout the text. References are mainly to the literature, with scant attention to the numerous patents in this field.

The book unfortunately has several defects. The

description of surface-tension measuring methods is quite inadequate. The subtitle of the book would lead one to expect a compilation of experimental data and a discussion of the implications of physical measurements in practical applications. The propriety of including three sections from the well-known "Wetting and Detergency Symposium" is questionable, especially since this material is not properly integrated into the text.

Despite these deficiencies, the book will be useful in supplying information on commercially available compounds, in providing a check list of potential uses within an industry, and in indicating the usefulness of surface-active agents in processes which might be unfamiliar to the reader.

The Electron Microscope. 2nd Ed. E. F. Burton and W. H. Kohl. New York, Reinhold Publishing Corp., 1946. 325 pages. Price, $4.00.

(Reviewed by R. E. Rundle)

This description of the electron microscope is intended for the layman. Almost half of the book is devoted to a discussion of light, the light microscope, and the electron and wave-particle duality. Most scientists, even outside the physical sciences, will find the discussion rather superficial. The fact that it must be of help to the layman is probably best attested by the appearance of this second and enlarged edition so soon after the first edition (1942).

There are useful descriptions of the principles of electrostatic and magnetic electron optics, accompanied by illustrations which, though they vary a great deal in their pertinence, are generally effective. The historical section on the development of the microscope is a bit brief, and perhaps is excusably biased toward Toronto developments.

The chapter on applications is interesting, but it is not critical, and it is hardly inspiring in its consideration of the future of the electron microscope. The book contains throughout a large number of excellent reproductions of electron photomicrographs, which do much to add to its value.

Hackh's Chemical Dictionary. 3rd Ed. Edited by Julius Grant. Philadelphia, Blakiston Co., 1946. 925 pages. Price, $8.50.

The third edition of this well-known encyclopedic dictionary has been revised and edited in the light of new research findings.

Based on the very latest scientific data, it covers not only the terms used in general chemistry, but also the collateral vocabularies of physics, astrophysics, geology, mineralogy, botany, zoology, medicine, pharmacy, and the pertinent terms of industry, mining, and commerce.

It gives clear, brief statements of the theories, rules, and laws of chemistry. There are accurate descriptions of elements, compounds, drugs, minerals, and vegetable and animal products. Chemical apparatus, equipment, and instruments are included, and the names of scientists who have contributed to the progress of chemistry are likewise noted. Here will be found the latest data on atomic disintegration.

Practical Textile Designing. Thomas Nelson. Charlotte, N. C., Clark Publishing Co., 1945. 168 pages. Price, $1.25.

Prepared by Dean Nelson of the North Carolina State College School of Textiles, *Practical Textile Designing* clearly describes the principal types of weaves in use today by the textile industry.

Accompanying the descriptive matter are illustrations of the weave design and photographs of typical fabrics employing the weaves.

This little book should be valuable both to the student and as a reference work for the trade.

ABSTRACTS

SERVICES AVAILABLE

Reprints of the original articles abstracted in TEXTILE RESEARCH JOURNAL *are often available from the publishers. Otherwise, it may be possible to secure copies of the periodicals. Orders should be sent direct to the publishers.*

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Subscriptions to reprints of the Abstracts section for Volume 16, 1946, are now available to subscribers to the JOURNAL. *These are printed on one side of the sheet for clipping and filing in a card index system. The charge for this service is $3.00.*

A list of periodicals, the abbreviations used in references to articles, and the addresses of publishers of English language publications is given on page 84 of the February, 1946, issue.

ANALYSIS: TESTING: LABORATORY METHODS

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Infra-Red Absorption Spectroscopy

Analysis of multicomponent mixtures of hydrocarbons in the liquid phase by means of infra-red absorption spectroscopy. D. L. Fry, R. E. Nusbaum, and H. M. Randall. *J. Applied Phys.* **17**, 150–61 (Mar. 1946).

The use of infra-red absorption spectroscopy in the analysis of liquid hydrocarbon mixtures is discussed, and a method for making this type of analysis is described. Absorption data on representative 4- and 5-component systems are converted to concentrations by either a graphical or a mathematical procedure. The authors state that a complete analysis on a 5-component mixture of the type studied may be obtained in less than 45 min. Analytical errors are of the order of 0.5% of the total sample.

Text. Research J. June 1946 T. J Dietz

Determination of Flexural Strength of Glass

Wide-range static strength-testing apparatus for glass rods. T. C. Baker and F. W. Preston. *J. Applied Phys.* **17**, 162–70 (Mar. 1946).

An apparatus for the strength-testing of glass rods in flexure is described. The device utilizes the modified driving assembly of a dynamic loud-speaker as a means of applying stress to the test specimen. With this design, it is possible to exert maximum stress in as short a time as 2 to 3 m.secs. The authors discuss the operation of the apparatus and the instrumental errors involved. T. J. Dietz

Text. Research J. June 1946

Stress-Strain Machine

A fast stress-strain machine. S. L. Dart, R. L. Anthony, and P. E. Wack. *Rev. Scientific Instruments* **17**, 106–8 (Mar. 1946).

A fast stress-strain machine for the study and testing of rubberlike materials is described. The machine is of simple design and can be operated at speeds up to 200% extension per sec. without serious error due to inertial effects. The complete stress-strain loop is recorded automatically. The reproducibility of the data obtained with this machine for a number of test specimens cut from the same tensile sheet is of the order of 1%. Authors

Text. Research J. June 1946

Yarn and Fabric Testing

Testing of yarns and fabrics. N. Eyre. *Text. Mfr.* **72**, 154–7 (Mar. 1946).

A description of methods for the determination of denier, testing of single-strand strength on the pendulum-type machine and on the inclined-plane tester, and testing by a ballistic machine which breaks several strands of yarn simultaneously under impact. The article relates specifically to the testing of filament yarns. H. J. Burnham

Text. Research J. June 1946

CHEMICAL AND PHYSICAL RESEARCH

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Absorption of Acids by Wool

Absorption of acids by wool. P. Larose and A. S. Tweedie. *Ann. ACFAS* **7**, 82 (1941). **Absorption of bases by wool.** *Ibid.* 83—cf. Harris and Rutherford, *C.A.* **33**, 5009[7] (through *Chem. Abstr.* **40**, 1320[9] (Mar. 10, 1946)).

Wool absorbs 0.25 equivalent of chloroacetic acid per 100 g. and 0.082 equivalent of HCl at or below pH 1. The absorption is reversible.

Text. Research J. June 1946

Absorption Spectra of Dyes

The absorption spectra of the negative ions of two diaminotriphenylmethane dyes. Bert M. Tolbert and Gerald E. K. Branch. *J. Am. Chem. Soc.* **68**, 315–19 (Feb. 1946).

The absorption spectra of the quinoidal negative ions of viridine green and 3,3′-dicarbazylphenylmethyl chloride have been measured in acetone solution. The spectra of the quinoidal negative ion of the carbazyl derivative show a strong band at 727 mμ and a weak band at 430 mμ. The negative ion of viridine green shows a strong band at 704 mμ but the existence of another band could not be shown owing to absorption by unneutralized anhydro base. The greater instability of the quinoidal negative ions as compared to the quinoidal positive ions has been discussed.

Text. Research J. June 1946 Authors

Electron Micrographs of Ground Cellulose

Macromolecular compounds. CCCXV. Cellulose. 87. Investigation of ground cellulose fibers with the electron microscope. E. Husemann and A. Carnap. *J. makromol. Chem.* **1**, 158–67 (1944); cf. *C.A.* **38**, 1107[9] (through *Chem. Abstr.* **40**, 201[2] (Jan. 10, 1946)).

Dry grinding of degraded wood pulp fibers in the oscillating mill leads, in contrast to earlier results by Hess, *et al.* (*C.A.* **36**, 1490[9]), to much-deformed fragments with only occasional appearance of fine fibrils when observed under the electron microscope. Pronounced fibrillation, however, is produced by wet grinding in either an agate ball mill or an oscillating mill. The degree of polymerization (D.P.) of a pulp was reduced from 700 to 500 in 6 hrs. and to 430 after 23 hrs. After 40 hrs. of grinding, the D.P. of cotton was reduced from 1960 to 1040 and of ramie from 1667 to 680. In contrast to results with hydrolytically degraded materials, no short fragments were detectable. Distinctly less fibrillation was observed with ground rayon fibers; after 23 hrs. the D.P. of cuprammonium rayon was decreased from 510 to 320, and of viscose staple fiber from 310 to 230.

Text. Research J. June 1946

Molecular Weight of Cellulose

The molecular weight of cellulose. O. P. Golova. *Trudy Konferentsii Vysokomolekulyar. Soedineniyam, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk i Otdel. Fiz.-Mat. Nauk* **1**, 29–30 (1943) (pub. 1945) (through *Chem. Abstr.* **40**, 457[8] (Jan. 20, 1946)).

Previous determinations of the molecular weight of cellulose dissolved in Schweizer's solution are incorrect, since removal of 0 from the solution was incomplete. When 0 is removed by He instead of N in a special apparatus (which is not described) a molecular weight of 8,000–10,000 is obtained. Formation of cellulose esters, even under very mild conditions, breaks down the macromolecule and cannot be used for determining the molecular weight.

Text. Research J. June 1946

Molecular weight of cellulose. O. P. Golova and V. I. Ivanov. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* **1945**, 279–81 (in Russian); cf. *C.A.* **40**, 457[8] (through *Chem. Abstr.* **40**, 1653[9] (Mar. 20, 1946)).

The presence of even very small amounts of O has a strong effect on the results of determinations of the molecular weight of cellulose by the usual methods (viscosity, diffusion, ultracentrifuge sedimentation) because of the cracking action of O on cellulose. Traces of O in the N used for the determinations and of that adsorbed in the cellulose fibers considerably lower the apparent molecular weight. In the present of O in amounts of 4.8×10^{20}, 3.5×10^{15}, 3.57×10^{13} and 3.57×10^{6} mol./cc., determination of molecular weight of cotton cellulose by viscosity in cuprammoniacal solution gave 50–60, 1500–1700, 4000–4200, and 9500–9800 for the number of glucose residues in the chain, and 9.72×10^{3}, 2.754×10^{5}, 6.804×10^{5} and 1.58×10^{6} for the molecular weight, respectively. Stringent purification resulted in an O content as low as 3.5×10^{4} mol./cc.; under these conditions the degree of polymerization of cotton cellulose was 9500–10000 glucose residues. As it is impossible to eliminate the last traces of O from the fibers, the only way of correct determination of the true molecular weight is graphic extrapolation to zero O content. This gave for native cotton cellulose, as a lower limit, 15000 glucose residues in the main valence chain, hence a molecular weight of at least 2430000–2592000.

Text. Research J. June 1946

Degree of Polymerization of Cellulose

The macromolecular structure of cellulose. I. Degree of polymerization. A. Munoz Hernández, E. Blanchard Castillo, and A. Lamana Pola. *Ion* **5**, 643–7 (1945) (through *Chem. Abstr.* **40**, 2298[4] (Apr. 20, 1946)).

An apparatus for determining molecular weights by the Staudinger method is described. Results are given for cellulose from 17 different sources.

Text. Research J. June 1946

Preparation of Cellulose Acetate

Preparation of cellulose acetate. Carl J. Malm, Leo J. Tanghe, and Barbara C. Laird. *Ind. Eng. Chem.* **38**, 77–82 (Jan. 1946).

The amount of combined sulfur has been determined at all stages in the manufacture of cellulose acetate, including pretreatment, acetylation, and hydrolysis. Little combined sulfur was found during the pretreatment; but after the addition of acetic anhydride, the sulfuric acid combined quantitatively with the cellulose in the intermediate stages of acetylation. At the point where substantially all the hydroxyl groups had been esterified, the combined sulfur content began to drop gradually, and as the reaction time was extended beyond the point where it is normally interrupted to

initiate the hydrolysis stage, it continued to drop and was replaced by acetyl. The combined sulfur dropped rapidly during the addition of water for hydrolysis. The lowering of the sulfur content was sharply influenced by the temperature and the rate of addition of water. The amount of sulfuric acid catalyst was varied over a 32-fold range, and the amount of combined sulfur at the completion of esterification and during hydrolysis was roughly proportional to the concentration of sulfuric acid used. When part of the sulfuric acid was neutralized at the start of hydrolysis, the amount of combined sulfur in the product was determined by the amount of soluble sulfate (SO_4—) present during hydrolysis. Authors

Text. Research J. June 1946

Colloids

Monodispersed hydrophobic colloidal dispersions and light-scattering properties. I. Preparation and light-scattering properties of monodisperse colloidal sulfur. Victor K. LaMer and Marion D. Barnes. *J. Colloid Sci.* **1**, 71–7 (Jan. 1946).

Colloidal dispersions of uniform particle size were prepared by adding $Na_2S_2O_3$ solution to a very dilute H_2SO_4 solution. Particles grew in size over a period of 24 to 30 hrs. The growth was stopped by titrating the unreacted thiosulfate with iodine. Proof that the sols were uniform in particle size is shown by the following: (1) the spheres all had same brightness in the ultramicroscope without any twinkling, (2) large particles were uniform spheres in the light microscope, and (3) all particles of a given sol had the same color under the microscope. The sols of small particle size exhibited the optical properties predicted by the Rayleigh equation, but with sols of larger particle size, higher order effects, characterized by the dispersion of the scattered light in bands (or spectra) of different colors whose intensity, polarization, and angular distribution depend on particle size, were observed. E. D. Klug

Text. Research J. June 1946

Monodispersed hydrophobic colloidal dispersions and light-scattering properties. II. Total scattering from transmittance as a basis for the calculation of particle size and concentration. Marion D. Barnes and Victor K. LaMer. *J. Colloid Sci.* **1**, 79–91 (Jan. 1946).

Accurate determinations of the total scattering curves for various particle size were made over the range of wave lengths from 275 mμ to 600 mμ for a system of monodispersed sulfur particles in water. The form of the transmittance curve as predicted by the Mie theory of the scattering of light by colloidal particles has been experimentally verified in detail. The diameter and concentration of the particles were calculated from the transmittance as a function of wave length. The nature of the total scattering has been experimentally determined in a range of α values ($\alpha = 2\pi r/\lambda'$) wherein it has been too difficult to calculate it. Authors

Text. Research J. June 1946

Emulsions

Emulsions and their applications to textiles. H. A. Neville. *Am. Dyestuff Reptr.* **34**, P534–6 (Dec. 17, 1945).

The nature of emulsions and the chemical, physical, and mechanical conditions favorable to the formation of both oil-in-water and water-in-oil types are discussed. If the conditions for formation of the interfacial film (from the emulsifying agent) are ideal, emulsification will be practically spontaneous on mixing the 2 phases; in practice, intermittent shaking or agitation is found to be more effective in producing an emulsion than continuous action. Emulsions may be utilized to (1) economize on materials, (2) control concentration to obtain desired effect without causing damage, (3) modify such properties as flammability, odor, taste, texture, and viscosity, and (4) obtain increased reactivity owing to the extensive interfacial area existing in an emulsion. Because of the high surface-volume ratio common to all textile materials, emulsions may often be particularly appropriate in this field. K. S. Campbell

Text. Research J. June 1946

Carbohydrate Phosphoric Esters

Carbohydrate phosphoric esters. Part I. The alkaline hydrolysis of α-methylglucopyranoside-6-phosphate, methylglucofuranoside-3-phosphate, and isopropylidene glucofuranose-3- and 6-phosphates. E. E. Percival and E. G. V. Percival. *J. Chem. Soc.* **1945**, 874–6 (Dec. 1945).

The alkaline hydrolysis of the barium salts of the above carbohydrate phosphoric esters was studied and in no case was any evidence found of Walden inversion. Authors

Text. Research J. June 1946

Elastic and Plastic Flow

Structural processes in the flow of high polymers. V. A. Kargin. *Trudy Konferentsiĭ Vysokomolekulyar. Soedineniyam, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk i Otdel. Fiz.-Mat. Nauk* **1**, 10 (1943) (pub. 1945); cf. *C.A.* **37**, 1639[4] (through *Chem. Abstr.* **40**, 266[3] (Jan. 20, 1946)).

The distinction between reversible elastic deformation and irreversible plastic flow in high polymers is pointed out. The latter process changes the relation of various parts of the polymer to one another, and if the polymer contains many different groups, as do proteins, it may greatly modify the orientation and properties of the polymer chains.

Text. Research J. June 1946

Rubberlike Elasticity

A new approach to the theory of rubberlike elasticity. Maurice L. Huggins. *J. Polymer Research* **1**, 1–14 (Jan. 1946).

It is shown that for a simple, hypothetical model substance, containing like, independent systems, each capable of existing in two alternative orientations, stress-strain curves may be computed which are similar in form to those ordinarily

obtained from rubber and rubber-like materials, provided one introduces a certain dependence of the volume shift per rearrangement on the elongation. With this model, the dependence of the initial elastic modulus and that of the shape of the stress-strain curve on various characteristics of the rearranging systems are readily studied. Author

Text. Research J. June 1946

Effect of Water on Strength of Glass

The effect of water on the strength of glass. T. C. Baker and F. W. Preston. *J. Applied Phys.* **17**, 179–88 (Mar. 1946).

The flexural strength of glass rods immersed in various media was measured with the testing apparatus described in an earlier paper by the same authors (*J. Applied Phys.* **17**, 162–70 (Mar. 1946)). It was observed that the so-called strength of glass is adversely affected to a marked degree by water. When glass is exposed to moisture for 24 hrs., its strength may decay to $\frac{1}{3}$ of that observed for a control specimen which has been conditioned and tested in high vacuum. When the glass rods are treated with steam under pressure (600 lbs./sq. in.), the loss in strength is even greater. T. J. Dietz

Text. Research J. June 1946

Characterization of Keratin

Physicochemical characterization of dispersed chicken-feather keratin. Wilfred H. Ward, Loretta M. High, and Harold P. Lundgren. *J. Polymer Research* **1**, 22–36 (Jan. 1946).

Reduced chicken-feather keratin forms a soluble complex in neutral aqueous sodium alkyl benzene sulfonate (average: dodecyl benzene sulfonate). The chemical composition, specific refractive increment, partial specific volume, electrophoretic mobility, osmotic pressure, diffusion constants, and ultracentrifugal sedimentation of the complex have been studied. The complex is heterogeneous, but similar in general properties to egg albumin-sodium alkyl benzene sulfonate mixtures previously studied, including fiber-forming properties, the average molecular weight of the dispersed protein units, and the relative symmetry of the dispersed units in dilute solution. Authors

Text. Research J. June 1946

Effect of Ultraviolet on Cellulose Acetates

The action of ultraviolet light upon cellulose and cellulose triacetate. E. Heuser and George N. Chamberlin. *J. Am. Chem. Soc.* **68**, 79–83 (Jan. 1946).

When cellulose is irradiated by ultraviolet light in helium, the same results are obtained as were previously reported for irradiation in nitrogen (*ibid.* **66**, 753 (1944)). This would appear to rule out the hydrolysis of cellulose by oxides of nitrogen formed from the small amount of oxygen not evacuated. The same post-irradiation effect occurred when either helium or nitrogen was used. In the case of cellulose triacetate, the reducing power and acetyl content remain unchanged when irradiated in helium or nitrogen but in oxygen, far-reaching deacetylation occurs and the copper number and uronic acid content increase considerably. The latter would indicate that the hydroxyl on carbon 6 was oxidized. Cellulose triacetate irradiated in helium or nitrogen, then stored in air or oxygen, shows the same post-irradiation effect as cellulose. This would seem to indicate that ultraviolet irradiation weakens the glycosidic linkages so that they are more susceptible to oxidation but does not affect the hydroxyl groups.

A. R. Macormac

Text. Research J. June 1946

Cotton Pectin

Pectin of cotton. P. Larose and F. Leger. *Ann. ACFAS* **7**, 83 (1941) (through *Chem. Abstr.* **40**, 1320[8] (Mar. 10, 1946)).

Pectin represented all of the non-α-cellulose portion of cotton. Removal of the pectin did not alter the viscosity of the cuprammonium solution of cotton. There was no indication of a chemical difference between the interior and exterior pectins of the fiber.

Text. Research J. June 1946

Degradation of Pectin

The thermal degradation of pectin. Reynold C. Merrill and Mary Weeks. *J. Am. Chem. Soc.* 67, 2244–7 (Dec. 1945).

The large initial decrease in viscosity of pectin solutions on heating is due mainly to the breaking of primary chemical valence bonds rather than to the destruction of a secondary aggregate. This is shown by the irreversibility of degradation, the absence of a pronounced effect of urea and temperature on the viscosity of dilute pectin solutions, the fact that the loss in relative viscosity is closely associated with a decrease in the intrinsic viscosity of the pectin, and the magnitude of the value for the activation energy of the loss in viscosity with heating time.

Text. Research J. June 1946 Authors

Cohesive Forces in Plastics

Some principles underlying the behavior of plastics. Jerome Alexander. *Colloid Chemistry* **6**, 855–9 (1946) (through *Chem. Abstr.* **40**, 2352[9] (Apr. 20, 1946)).

Most commercial plastics are co-dispersions; that is, they consist of mixtures of substances whose basic particles may vary greatly in order of magnitude. The forces affecting the particles are (1) aggregative forces tending to form larger aggregates or units with new properties; (2) dispersive forces, tending to separate units (*e.g.*, attraction of solvent molecules, thermal and mechanical agitation); (3) protective action (*e.g.*, of adsorbed layers). The nature and strength of the forces vary with the size of the units considered, running from chemical bonds, cohesion and adhesion, to mechanical interlocking. The functioning of a clinch-nail or of a rivet, though it involves cohesion, is not understandable in terms of cohesion alone. Fiberglas is considered.

Text. Research J. June 1946

Polymerization

Reactivity as a function of chain length. Turner Alfrey and Edmund Merz. *Polymer Bull.* **1**, 69–71 (Aug. 1945).

In analysis of both polycondensation and vinyl polymerization, it is assumed that the reactivity of a terminal group is independent of chain length. Since there is some evidence that this is not so, equations are derived, assuming that reactivity is a function of chain length. Suitable experimental distribution curves for applying these equations are not available.

Text. Research J. June 1946 E. D. Klug

Mechanism of Polymerization

Organic chemical aspects of high polymers. W. P. Hohenstein. *Polymer Bull.* **1**, 60–8 (Aug. 1945).

A review of the mechanism of addition polymerization and condensation and of the structure of the polymers. E. D. Klug

Text. Research J. June 1946

Copolymerization

Experimental study of copolymerization. T. Alfrey, E. Merz, and H. Mark. *J. Polymer Research* **1**, 37–43 (Jan. 1946).

Copolymerizations of (1) styrene and dichlorostyrene, (2) methyl acrylate and styrene, (3) styrene and diethyl maleate, and (4) styrene and diethyl chloromaleate were carried out under conditions such that low degrees of conversion (less than 5%) were obtained. The compositions of polymers were determined by analysis for chlorine or carbon and hydrogen. The values of α and β, the ratios of reaction rate constants, were determined from the data. E. D. Klug

Text. Research J. June 1946

Vinyl Polymerization

Some results of vinyl polymerization in solution. D. Josefowitz and H. Mark. *Polymer Bull.* **1**, 140–55 (Dec. 1945).

The rate of polymerization R during the initial stages (2 to 15% polymerization) was determined for the following systems: (1) styrene in toluene with benzoyl peroxide at 25°C and 47.5°C, (2) styrene in toluene with tetraphenyl-succinodinitrile at 63.5°C and 100°C, (3) vinyl acetate in methyl ethyl ketone with benzoyl peroxide at 25°C and 50°C, and (4) isoprene in toluene with benzoyl peroxide at 72°C and 100°C. R was found to be proportional to the square root of the catalyst concentration. At constant catalyst concentration the relationship between R and the monomer concentration m was $\frac{m^3}{R^2} = Km + k$ for styrene in toluene. This equation is derived on the assumption that the monomer first reacts with a molecule of catalyst to bring about activation and then reacts with radicals to bring about propagation. The effect of an activator (sodium bisulfite) in the peroxide-catalyzed vinyl acetate polymerization is to increase the rate but not the degree of polymerization. E. D. Klug

Text. Research J. June 1946

Mechanism of vinyl polymerizations. VIII. Introduction of foreign end groups. Charles C. Price and David H. Read. *J. Polymer Research* **1**, 44–8 (Jan. 1946).

Polymerization of styrene in the presence of dichlorohydroquinone and dichlorobenzoquinone proceeded to form about the same amount of polymer as parallel polymerizations in the absence of these materials. The molecular weight was lower, however, so that these compounds act primarily as chain transfer agents, like chloranil and not as inhibitors like benzoquinone. Styrene polymerizations with *p*-bromobenzoyl peroxide as a catalyst and nitrobenzene, dinitrobenzene or nitrothiophene as retarders gave 2 to 4 times the number of retarder fragments as catalyst fragments in the resulting polymers. This behavior is ascribed to weak chain-transfer characteristics of the retarder molecules. E. D. Klug

Text. Research J. June 1946

High-Polymer Crystallization

Equilibria and rates in crystallization of high polymers. Turner Alfrey. *Polymer Bull.* **1**, 40–6 (June 1945).

A discussion of the kinetics and thermodynamics of high-polymer crystallization. No new data.

Text. Research J. June 1946 E. D. Klug

Elastic Moduli of Rubberlike Polymers

Molecular processes during deformation of rubberlike elastic bodies. Kurt H. Meyer and A. J. A. Van Der Wyk. *J. Polymer Research* **1**, 49–57 (Jan. 1946).

The elastic moduli of slightly degraded rubber, Buna (butadiene-sodium polymer), vulcanized butadiene-acrylonitrile copolymer, polyisobutylene, elastic sulfur, and elastic fiber from animal tissue (ox ligament) were determined at elongations of 5 to 20%. From these data, as well as from some of previous workers, no relationship between elastic modulus and molecular weight or average weight of the chain fragment between 2 cross links was evident. The authors believe that relationships between molecular weight and elastic modulus derived by other workers are unsound in that they assume (1) that the deforming force attacks the linear polymers only at the ends of chains and net polymers only at the cross links and (2) that the gaseous state can be taken as a basis for calculations for the rubberlike state.

Text. Research J. June 1946 E. D. Klug

Styrene Polymers

Mechanism of peroxide-initiated styrene polymerization. Infrared absorption of some polymer samples, Harry F. Pfann, Van Zandt Williams, and H. Mark. *J. Polymer Research* **1**, 14–21 (Jan. 1946).

Polystyrene was prepared by heating styrene with and without *m*-bromobenzoyl peroxide in a sealed glass tube at 140°C. The infrared absorption at 1720 cm^{-1} and 1250 cm^{-1} increased with the con-

centration of peroxide used to bring about polymerization and with the halogen content of the polymer, but decreased with increase in molecular weight (viscometric or osmometric). At 1380 cm^{-1} the infra-red adsorption was constant irrespective of the temperature of polymerization or concentration of polymerization catalyst. It is concluded that these data support previous chemical evidence of the existence of benzoate esters groups in the polymer molecule. E. D. Klug

Text. Research J. June 1946

Polymer Surface Films

Surface films in polymers. D. J. Crisp. *J. Colloid Sci.* **1**, 49–70 (Jan. 1946).

The uniformity of films of various polymers at the water-air or oil-water interface was determined by observation under dark-field illumination. The polymers of least internal cohesion, polyvinyl acetate and polyacrylates, spread most easily. The specific area occupied per monomer unit for various molecular weight fractions of polyvinyl acetate was independent of the molecular weight. The force-area curves for polymethyl, polyethyl, polyisopropyl, and poly-*n*-butyl acrylate and for various polyvinyl alcohol-aldehyde condensates (Formvar, Alvar, etc.) were determined. Estimations of the specific areas are in reasonable agreement with known molecular dimensions and probable molecular configurations.

Text. Research J. June 1946 E. D. Klug

Thermodynamics of High Polymers

Thermodynamics of high polymer solutions. Maurice L. Huggins. *Polymer Bull.* **1**, 25–30 (June 1945).

High-polymer solutions show very large deviations from Raoult's law—much larger than can be accounted for by the changes in heat content. An expression is derived for the activity of a large chain molecule dissolved in a solvent of small molecules. This equation is in good agreement with experimental data. From osmometric data, the activity can be calculated.

Text. Research J. June 1946 E. D. Klug

Borated Resins

Borated resins. Ernest P. Irany. *Colloid Chemistry* **6**, 1089–92 (1946); cf. *C.A.* **38**, 1295[7] (through *Chem. Abstr.* **40**, 2350[7] (Apr. 20, 1946)).

Boric acid tends to form complex products with polyhydroxy compounds. Polyvinyl acetals and cellulose esters and ethers are greatly affected by even minute additions of boric acid. Various uses are suggested.

Text. Research J. June 1946

Ion-Exchange Resin

Improved synthetic ion-exchange resin. W. C. Bauman. *Ind. Eng. Chem.* **38**, 46–50 (Jan. 1946).

An improved cation-exchange resin of the phenolformaldehyde type containing nuclear sulfonic acid groups is now available to the industry. The exchange capacity of this resin is shown to be higher than previously known cation-exchange materials in both sodium and acid cycles. The resin is stable and without color throw over a wide range of pH up to 100°C and shows excellent stability to rapid changes in salt concentration. Field tests on the material have been run on both water softening and demineralization for three years. Photograph shows the operating floor of a purification plant for boiler feed water.

Text. Research J. June 1946 Author

Resonance Theory

A discussion of reduction by aqueous sodium sulphide and the application of resonance theory to the selective monoreduction of the αβ-dinitronaphthalenes. H. H. Hodgson. *J. Soc. Dyers and Colourists* **61**, 171–2 (July 1945).

The preferential monoreduction of the α-nitro- group in a heteronuclear αβ-dinitronaphthalene by acid stannous chloride and of the β-nitro-group by alkaline sodium sulfide are explained from the standpoint of the resonance theory on data based on absorption spectra. The mechanism of reduction of a nitro- group by sodium sulfide is discussed. Author

Text. Research J. June 1946

Rubber from Furfural

The production of rubber from furfural. L. W. Burnette. *Rubber Chem. Tech.* **18**, 284–5 (Apr. 1945).

The conversion of furfural to piperylene through methylfurane (sylvane) and tetrahydrosylvane is described; data on yields and approximate costs are given. The use of piperylene to produce a synthetic rubber is suggested. W. E. Davis

Text. Research J. June 1946

Mastication of Rubber

Mastication and rate of setup. Part II. S. Buchan. *Rubber Chem. Tech.* **18**, 441–7 (Apr. 1945).

Several factors were investigated as possibly influencing the decrease in rate of setup which accompanies longer milling of rubber. They included the decomposition of accelerators, softening of the rubber due to mechanical working, breakdown of rubber particles, depolymerization, and oxidation. The last process was found to be the most important; attempts to catalyze the oxidation by addition of copper in various forms were unsuccessful, and it was found that copper was an accelerator of depolymerization rather than of oxidation.

Text. Research J. June 1946 W. E. Davis

Oxidation of Rubber

Antioxidant influence of sulfur in mastication of rubber. Research Assn. of British Rubber Mfrs. *Rubber Chem. Tech.* **18**, 438–40 (Apr. 1945).

It is shown that although sulfur is a negative catalyst for the type of oxidation which produces surface tackiness in raw rubber exposed to light, it does not inhibit the oxidation, which is the essential factor in mastication of rubber on the mixing mill. W. E. Davis

Text. Research J. June 1946

"Turret"-Type Ultracentrifuge

Studies on sedimentation velocity and diffusion rate of linear high polymers. K. G. Stern, Seymour Singer, and Sanford Davis. *Polymer Bull.* **1**, 31–9 (June 1945).

A description of the air-driven, "turret"-type ultracentrifuge at the Brooklyn Polytechnic Institute. Schlieren diagrams for a cellulose acetate fraction and for polyvinyl chloride are shown. The rate of diffusion was measured in a Tiselius apparatus, and schlieren diagrams taken during the diffusion of a cellulose acetate fraction are given.

Text. Research J. June 1946 E. D. Klug

Filtering Properties of Viscose

The filtering properties of viscose. Olof Samuelson. *Svensk Papperstidn.* **48**, 517–27 (1945) (in English) (through *Chem. Abstr.* **40**, 1998[9] (Apr. 10, 1946)).

Hermans and Bredée (*C.A.* **29**, 6801[6]) discussed the law of cake filtration, representing a measure of the rate of blocking of a filter by liquids containing a relatively large quantity of precipitate. Spruce sulfite pulp intended for the manufacture of viscose was used in the present experiments. The rate of blocking of viscose increases with increasing viscosity and decreasing ripening period, unless the mechanical agitation of the viscose during xanthation is very intensive. When the filtering properties of 2 viscose solutions (prepared under different conditions) are to be compared, it is essential to keep their viscosities uniform. This was attained in this study by altering the length of the period allowed for the ripening process. The filtering properties of viscose are determined as a function of the quantity of CS_2 (or NaOH) present in the viscose after xanthation under varying conditions. These properties are considerably poorer when the quantity of CS_2 or NaOH falls below a certain value. On intensive mechanical agitation, smaller quantities of chemicals are required than with poor agitation. With large additions of CS_2 or NaOH, the filtering properties no longer depend upon mechanical agitation. Samuelson discusses the reasons for the blocking of the filter and considers particularly the micellar structure of the viscose. The cellulose xanthate in a viscose solution diluted with NaOH is considered to be present in a molecular dispersed form, regardless of the filtering properties of the viscose. 39 references.

Text. Research J. June 1946

Viscosity

Dilute solution viscosity of heterogeneous high polymers. R. S. Spencer and R. F. Boyer. *Polymer Bull.* **1**, 129–39 (Dec. 1945).

The slope of the straight line obtained by plotting viscosity/concentration against concentration for solutions of low concentration is shown both theoretically and experimentally to increase with the heterogeneity of the polymer. The heterogeneity coefficient of a polymer sample is defined as the ratio of the slope of the above-mentioned line to the slope of the line for the corresponding homogeneous polymer. Expressions are derived for the heterogeneity coefficient for the special case of a mixture of 2 similar polymer fractions and for certain molecular-weight distributions. With accurate weight-average and number-average molecular weights and the heterogeneity coefficient, it is possible to determine the 2 constants for the intrinsic viscosity-molecular weight relationship. The constants, calculated for a sample of polystyrene in toluene, are in fair agreement with the observed values.

Text. Research J. June 1946 E. D. Klug

Viscosity of Dilute Solutions

Dependence of viscosity on velocity gradient in very dilute suspensions and solutions. Werner Kuhn and Hans Kuhn. *Helv. Chim. Acta* **28**, 97–127 (1945) (in German) (through *Chem. Abstr.* **40**, 789[3] (Feb. 20, 1946)).

The axes of geometrically anisotropic particles, suspended in solution and subjected to a velocity gradient, experience a partial orientation which in turn induces a directed Brownian motion of the particle axes. For change of free energy into heat this directed Brownian motion plays the same role as the directed motion taking place in a conservative force field. The starting postulates used by prior investigators to calculate the viscosity of colloidal suspensions are therefore incomplete, because that fraction of the frictional heat developed in the solution by diffusion was ignored. At very low velocity gradients, suspensions of long particles thus have about twice the specific viscosity calculated on the basis of the older, incomplete postulates. The extended theory yields viscosity values that decrease with increasing velocity gradient, a result in harmony with experience (so-called structural viscosity); earlier theories gave the opposite (incorrect) trend. The quantitative expression for viscosity of the suspension in terms of dimensions of suspended particles, viscosity of solvent, and velocity gradient are given for 4 types of model, 2-dimensional theory being used for the dumbbell and rigid rod, the general (or 3-dimensional) theory being used for rotational ellipsoids of both types.

Text. Research J. June 1946

Chemistry and Technology of Wool

The chemistry and technology of wool. I. Some relationships between the constitution, properties, and uses of wool. J. B. Speakman. *J. Roy. Soc. Arts* **93**, 603–13 (1945) and *Text. Recorder* **63**, 47–9 (Jan. 1946) and 49–52 (Feb. 1946).

The amino acid composition of wool varies considerably depending on the nutritional value of the pasture on which the sheep feed and varies along the fiber length. The cross-linkage within the fiber by cystine molecules, hydrogen bonding, van der Waals forces and salt linkages materially affects chemical and physical properties of wool. The combining capacity of wool for acid is determined mainly by the amount

of arginine and lysine present and in an acid dye bath, the primary reaction is with the rapidly diffusing inorganic acid, but, as boiling is continued, the inorganic anion is displaced by the slower-moving colored anion thus dyeing the fiber. By blocking or removing the basic side groups of wool, the fiber becomes more resistant to acid dyeing. This may be carried out in several ways, however, the reaction with glyoxal-bis-sodium bisulfite has proved to be satisfactory. Resist processes of this kind have increased the versatility of wool, making it possible to obtain a multitude of two-tone effects. The breakdown of the cystine linkage generally weakens the fiber and reduces its elasticity, thus damaging the fiber, though there are cases where benefits may be derived. As a result of disulfide bond breakdown, exposed wool swells to a greater extent, and with colloidal dyes the tip is dyed darker than the root, and vice-versa with crystalloidal dyes. By reforming the cystine cross-linkages with basic chromium acetate, level dyeing with acid and chrome dyes may be obtained. The main advantages in disulfide bond breakdown is found in the promotion and prevention of felting and milling shrinkage. To increase felting the "carroting" type of process is employed. The reagent most commonly used to reduce felting and shrinkage is an aqueous solution of chlorine. Further proof of the importance of disulfide bond breakdown in relation to unshrinkable finish has been obtained by comparing the action of chlorine, sulfuryl chloride, and sodium hydroxide on untreated wool and wool in which some of the disulfide bonds were replaced by more resistant cross-linkages. The permanent set which fabrics acquire on exposure to steam or boiling water is due to 2 consecutive intramolecular reactions: disulfide bond breakdown; followed by linkage rebuilding. Permanent set may also be obtained by 3 types of reagents: (1) oxidizing agents, (2) metal salts, and (3) organic dihalides. Internal polymerization of ethylene sulfide in wool increases wool's resistance to extension in water. The process can be carried out with monomeric vinyl and vinylidene compounds in general. Unshrinkability may be obtained by surface polymerizations with the use of such materials as anhydrocarboxyglycine which appears to be ideal for this purpose. As a result of studies of cross-linking and polymerization reactions in the keratin molecule, a series of new finishing processes for wool textile materials should emerge.

A. L. Merrifield

Text. Research J. June 1946

The chemistry and technology of wool. II. The x-ray interpretation of wool. W. T. Astbury. *J. Roy. Soc. Arts* **93**, 613–22 (1945) and *Text. Recorder* **63**, 44–6, 67 (Jan. 1946) and 53–63 (Feb. 1946).

The principle keratin x-ray diffraction patterns of wool are α-keratin and β-keratin; the former given by unstretched wool and the latter, stretched wool. The third fundamental pattern is that of steam-treated β-keratin. Stretching produces stressing in the cross-linkages which so raise their potential energy that they become susceptible to hydrolytic breakdown and which allows the stresses to be released by exposure to water or water vapor, known as "relaxation." Permanent set is produced by prolonged steaming of the stretched fiber whereby the structure is stabilized in the β-form. "Super-contraction" may be produced by short-time steaming of stretched fibers, releasing the strain, and resteaming. Subsequent x-ray investigations have revealed that keratin, myosin, fibrinogen, and fibrin are of a family in that they all have α-patterns and show α-β transformation on stretching, which tends to point to a common molecular plan based on the α-fold. This group, however, differ in their chemical components as their amino acid analyses are considerably different. The solution of the question, what it is in their respective chemical constitutions that determines the α-fold, rests in crystallographic and tensile data common to the whole group. The conditions to be met are given and discussed. The fold that satisfies these requirements in correct scale models is shown. The side chains in the protein should be close-packed; close-packing would not necessarily be in a regular manner except for another condition. The suggested further condition is that the side chains shall be alternately polar and non-polar. The fiber structure is built up by interactions between polar side chains down one side of a main chain and those down the opposite side of the next chain, and similarly for the van der Waals attractions between the non-polars, and so on. The difference between the various members of the group must lie, therefore, in which particular polar and non-polar residues are employed. If information can be obtained by exact chemical analyses carried out on the actual x-ray specimens, it might prove possible to deduce the sequence of residues along the chains. This knowledge obtained from x-ray studies of the fibrous proteins has led to the elucidation of the essential features of the structure of the crystalline proteins, and thence to the principles underlying the production of man-made protein fibers.

A. L. Merrifield

Text. Research J. June 1946

BLEACHING: DYEING: FINISHING

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Dyeing of "Rayolanda"

"Rayolanda": Dyestuffs and methods of dyeing. W. Penn. *Silk and Rayon* **20**, 227–9 (Feb. 1946).

A brief discussion of the dyes and the methods of dyeing "Rayolanda" is given. This fiber shows affinity not only for direct, sulfur, azoic, and vat dyes, but also for those classes of dyes normally employed for dyeing wool, such as acid, Neolan and Palatine, and chrome dyes. When blended with other fibers, tone-in-tone effects or solid shades may be obtained by proper selection of dyes and methods of dyeing. Level-dyeing acid dyes offer extremely bright shades of poor wash-fastness. Vat, soledon,

azoic, and sulfur dyes offer a fastness similar to that obtained by the same dyes on rayon and between these two extremes direct cotton, fast acid, chrome, and Neolan dyes supply ranges of good light- and wash-fastness combined with ease of application. A. L. Merrifield
Text. Research J. June 1946

Jig Dyeing

Dyeing methods for woven and knitted fabrics. Anon. *Silk and Rayon* **20**, 232–4 (Feb. 1946).

A brief discussion of the use of the jig in dyeing and ways to overcome some of the difficulties encountered, such as ending, uneven dyeing, excessive stretching, and undue pressure on the fabric during dyeing. A. L. Merrifield
Text. Research J. June 1946

Physical Chemistry of Dyeing

Physical chemistry of dyeing. E. I. Valko. *Colloid Chemistry* **6**, 594–619 (1946) (through *Chem. Abstr.* **40**, 2310[2] (Apr. 20, 1946)).

Physical chemistry of fibers and dyes; kinetics and equilibrium of the dyeing process; theory of dyeing; particle size of dyes on the fiber; level dyeing. 91 references.
Text. Research J. June 1946

Dyeing and Finishing Rayon

Notes on the dyeing and finishing of "Fibro." C. Wilcock. *Silk and Rayon* **20**, 100, 102 (Jan. 1946).

An important fact in rayon dyeing that is not generally appreciated is that more dye is required on a fine- than on a coarse-filament denier rayon to obtain the same depth of shade. It is possible to calculate the relative percentages of dye required by dividing the square root of one denier by the square root of the other denier. Low-denier yarns when dyed with direct cotton dyes are less fast to washing than coarse-filament rayons. This may be overcome, however, by after-treatment with "Fibrofix," which improves the fastness to washing, perspiration, desizing, acid cross-dyeing, water- and wet-finishing of dyeings made with direct cotton dyes. An outline of the method of producing dyed and crease-resistant fabrics is presented. Care must be given to the application of crease-resistant finishes as nonuniformity is produced by migration, variations in amount of resin, and degree of polymerization of the resin. These nonuniformities may be shown by staining the treated fabric with an azoic combination and confirmed by dyeing with a 2% solution of 20% Duranol violet, whereby the affinity for this dye is increased by the amount and degree of polymerization of the resin. By giving spun rayon fabrics a crease-resist treatment, the properties of the fabrics are altered as follows: increased recovery from creasing, a heavier cloth, increased fastness to washing of dyeings of direct cotton dyes, a fabric more stable to washing, improved dry and wet tensile strength, and lower water imbibition. A. L. Merrifield
Text. Research J. June 1946

Package-Dyeing Viscose

Developments in the package-dyeing of viscose rayon. H. A. Thomas. *Silk and Rayon* **19**, 1363–4, 1367 (Dec. 1945).

A discussion of package-dyeing of viscose rayon. The three main desiderata in package-dyeing are: (1) dyeing control which involves selection of dyes and use of appropriate conditions, including adjuvants in the dye liquor; (2) satisfactory form of package (they must be uniform but not tight; otherwise there is a poor flow of liquor); and (3) good flow of liquor. Pressure of circulation is not so important as the volume of dye liquor passing through the package, i.e., gals. per lb. of fiber per min. is of prime importance. A. L. Merrifield
Text. Research J. June 1946

Antimony Oxide for Flameproofing

Antimony oxide—its use as flame-resisting coating. C. C. Downie. *Paint Manuf.* **16**, 13–16 (1946) (through *Chem. Abstr.* **40**, 2009[5] (Apr. 10, 1946)).

Fresh markets have been found for Sb_2O_3 paints. They are useful for corrosion-resisting coatings, for marine uses, and in heat- and flame-resisting paints. A unique feature of Sb_2O_3 paints used during the war was their ability to resist flames which could scorch off most coating materials. The property is dependent on the fact that although the trioxide is volatile it can be reduced to metallic Sb in presence of organic matter, vehicles, etc., and secondly it can be converted to the stable tetroxide, as part of it will be oxidized to the pentoxide condition. When flame is projected onto a metallic surface coated with pigments of this variety, the metallic Sb so set free tends to combine to form a skin of antimonide and so continues to protect the underlying metal. Modern Sb paints are strongly resistant to strong acids, even HCl, which was formerly regarded as an attacking and dissolving material for Sb compounds.
Text. Research J. June 1946

Saponification of Acetate Rayon

Alkalis in the treatment of acetate rayon. Anon. *Silk and Rayon* **20**, 237, 239, 240 (Feb. 1946).

The advantages and disadvantages of saponification of acetate rayon are discussed. The saponification of acetate rayon increases the affinity of this rayon for direct cotton dyes, and part saponification may increase its affinity for acetate dyes. Saponification is usually uneven; however, barium hydroxide yields a more evenly saponified acetate rayon than does sodium carbonate or caustic soda and also the resulting rayon is more lustrous. It is evident that the action of alkalis on acetate rayon can be utilized advantageously or it can be a hindrance to dyeing and other wet processes. The exact action of the alkali is dependent on the particular alkali employed and the state of the rayon at the time of its application. A. L. Merrifield
Text. Research J. June 1946

Application of Oil to Wool

Chemical aspects of the application of dust-laying oils to wool. C. H. Bayley and A. S. Weatherburn. *Can. J. Research* **23F**, 402–12 (1945) (through *Chem. Abstr.* **40**, 2004[4] (Apr. 10, 1946)).

In the treatment of woolen blankets with dust-laying oils (for the purpose of reducing dust-borne infection) by the use of positively charged emulsions of oil in water, the rate of exhaustion of the treating bath is increased by (*a*) raising the temperature, (*b*) raising the pH, and (*c*) reducing the concentration of emulsifying agent to the minimum amount necessary for stable emulsification of the oil. Traces of soap remaining in the wool after laundering cause a reversal of the electric charge on the emulsion droplets and therefore prevent complete exhaustion of the treating bath. Suggestions are made regarding the practical application of the process.

Text. Research J. June 1946

Shrinkproofing Wool

Unshrinkable wool processes, with special reference to the treatment of wool materials containing rayon. Anon. *Silk and Rayon* **20**, 116, 118, 122–3 (Jan. 1946).

The advantages and disadvantages of the available processes for producing unshrinkable wool and their effect on wool-rayon mixtures are presented. These processes fall into three main groups: (1) those in which wet wool is treated with aqueous solutions of suitable reagents; (2) those in which the wool is first dried so as to contain a specified amount of moisture and is then treated with the reagent dissolved in an organic solvent or in a gaseous state; (3) those in which the wool is treated so that it becomes coated or impregnated with a resin or polymer of other similar substance. If the fabrics are required to have an especially soft and lofty hand, it is likely that nonfelting treatments will be left until the final stages of finishing; but when the textile material is required to have a smooth, clear-cut, thready appearance, then the treatment can usefully be effected before weaving or knitting. A. L. Merrifield

Text. Research J. June 1946

Sizing Rayon and Linen

Good sizing is an investment. W. J. MacNab. *Fibres, Fabrics and Cordage* **12**, 462–4 (1945) (through *Chem. Abstr.* **40**, 2312[3] (Apr. 20, 1946)).

Recipes and directions are given for the sizing of viscose spun rayon, spun acetate, and linen.

Text. Research J June 1946

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

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Animal Fibers

The growth and structure of animal fibers. A. B. Wildman. *Text. Mfr.* **72**, 149–51 (Mar. 1946).

A description of the physical structure and formation of various types of animal hairs and fibers. 7 references. H. J. Burnham

Text. Research J. June 1946

Nep Count

Counting neps in fibers. Horace L. Pratt. *Cotton* **110**, 72–6 (Mar. 1946).

Methods of counting neps in raw stock, sliver, roving, and yarn are described. For raw stock, 5 pinches of cotton of about 5 gr. each are put together and pulled into a "hand sliver" about 18 in. long. This is then broken down to a sample slightly longer than the staple length by repeated halving and doubling, care being taken to retain all of the fibers. Pinches of fibers are then pulled from the bundle and laid out on a velvet-covered board ruled off in 64 $\frac{1}{2}$-in. squares. Slightly less than 1 gr. of fibers is generally laid down and the neps counted under an inspectograph, which is simply a larger reading glass fixed in a frame and illuminated by fluorescent lights. It is said that higher magnification such as that obtained with the Readex makes it difficult to distinguish between a nep and a thick place in the array. After counting, all of the fibers (including neps) are removed from the board and weighed, and the result expressed in neps per gr. An uncovered board is used for a card web, the specimen being obtained by stopping the card and lifting a section of the web out, using a second board on top of the web. Drawing sliver and roving samples are made the same way as raw cotton samples, using a velvet-covered board. Yarn nep counts are made on blackboards with the strands of yarn spaced wide apart. Results are expressed in neps per 100 yds. Only defects coming under the A.S.T.M. definition of a "nep" are counted. H. J. Burnham

Text. Research J. June 1946

Wool on the Cotton System

Worsted yarns effectively spun on cotton frames. François A. Cleyn. *Textile World* **96**, 123, 206, 209 (Mar. 1946).

The making of worsted yarns employing long-draft cotton machinery is described. A tremendous development in this system is anticipated. Oil-combed tops weighing 50 gr. per yd. are used and a better fiber control makes possible higher drafts than can be achieved on the French or Bradford system. It is said that the resultant yarn is closer to French spun yarn than Bradford in appearance and that it can be used successfully wherever French spun yarn is used. The limitation is fiber length, 3 to 4 in. having been used successfully at the present time. Considerable saving in cost can be achieved, particularly with respect to reduction in number of operators involved and greater speed. Higher speeds are obtained because of less end-breakage, which is said to run as low as 25 breaks per 1,000 spindle hrs. H. J. Burnham

Text. Research J. June 1946

New Laundering Process

Influence of alkaline washing adjuncts in the laundering of materials of plant origin. A.

Schnijder. *Mitt. Textilind.* **50**, 131–3, 146–7, 158–9 (1943); **51**, 8–9, 22–3 (1944); *Tech. Wetenschapp. Tijdschr.* **13**, 262–3 (1944) (through *Chem. Abstr.* **40**, 2312[8] (Apr. 20, 1946)).

A plan for most effective laundering (minimum detergent, maximum washing effect, and minimum wear) of cotton, linen, and rayon is proposed. A preliminary (5–10 min.) steeping in pure water is followed by two passes through an alkaline-supported soap solution.

Text. Research J. June 1946

New Knitting Machine

A new interlock knitting machine. Anon. *Text. Recorder* **63**, 38–9 (Jan. 1946).

A new interlock knitting machine designed for simplicity, accessibility, ease of operation, and maintenance of high-quality fabric is described. The most important innovations are the new type of feed-wheel mechanism, increased number of feeders, and a patented draw-down mechanism. A. L. Merrifield

Text. Research J. June 1946

A.C. Motor Starters

Choice of A.C. motor starters. Anon. *Silk and Rayon* **20**, 120–1 (Jan. 1946).

The correct choice of motor control appliances is of great importance as this apparatus influences the starting conditions to a large degree. The merits of different types of apparatus for starting A.C. motors are reviewed. The requirements of a motor starter or controller are listed and curves show the starting torque and current required for two types of 3-phase squirrel-cage motors, star-delta starting of a fan load, starting with continuous-torque-star-delta starter, and starting of slip ring motors against full-load torque. A. L. Merrifield

Text. Research J. June 1946

The Center Filling Fork and Stop on Pick Motions

The center weft fork and the stop on pick motions. Anon. *Silk and Rayon* **19**, 1240–2 (Nov. 1945).

A discussion is presented of the construction and application to silk and rayon looms of the center filling fork and the stop on pick motions. Figures 1, 2, and 3 show the details of the center filling fork motion. The stop on pick motion embodies the "hit-and-miss" arrangement for the application of the brake and is shown in detail in Fig. 4. These types of filling and stop on pick motion can be fixed to the various types of negative looms, fast or loose reed machines.

A. L. Merrifield

Text. Research J. June 1946

WAR RESEARCH ON TEXTILES*

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U. S. Research

Footgear

Tests on footgear for trench foot. (Army Air Forces, Engineering Division, ENG-TSEAL-5H-3-157.) Benjamin Libet. O.P.B. Report PB 5102, 1945; 29 pp.; microfilm, 50¢—photostat, $2.00 (through *Bib. Sci. and Ind. Reports* **1**, 469 (Mar. 22, 1946)).

Trench foot is usually brought on by prolonged exposure of feet to wet cold above freezing. The wetness is important only in so far as it increases heat loss from the feet, mainly by lowering the insulative value of the footgear. The degree of warmth of the rest of the body, the amount of exercise done, and the tightness of fit of the footgear worn are important contributing factors. Footgear was tested to determine the thermal insulation. The tall cellular rubber and latex-silica-aerogel boots provide the most effective thermal insulation. Appendices present information on the trench-foot problem, test reports on thermal insulation of various footgear, and a report of a test which indicates the amount of wetting of footgear and cooling of feet that might be expected during activity in mud and water. Photographs.

Text. Research J. June 1946

* Copies of the original reports abstracted in this section may be obtained from the U. S. Department of Commerce, Office of the Publication Board, Washington 25, D. C.

Impregnation

Impregnation of herringbone twill with dimethyl phthalate and various fixatives. (Chemical Warfare Service T.D.M.R. 1115.) Shirley M. Glickman. O.P.B. Report PB 7240, 1945; 17 pp.; microfilm, 50¢—photostat, $2.00 (through *Bib. Sci. and Ind. Reports* **1**, 671 (Apr. 12, 1946)).

The object of the work described in this report was to impregnate herringbone twill with dimethyl phthalate (DMP) and various fixatives which might improve the persistance of the dimethyl phthalate. It was concluded that DMP-impregnated cloth is not made resistant to laundering, weathering, tropical conditions, or leaching by water by any of the fixatives used in the present work. Tables.

Text. Research J. June 1946

Clothing Insulation

Effective insulation of Army Air Force clothing. (Army Air Forces, Experimental Engineering Section, EXP-M-49-695-3.) A. P. Gagge. O.P.B. Report PB 6934, 1942; 21 pp.; microfilm, 50¢—photostat, $2.00 (through *Bib. Sci. and Ind. Reports* **1**, 469 (Mar. 22, 1946)).

Presents report on "the measurement of effective insulation on the human subject of current types of Air Force flying clothing," by the John B. Pierce Laboratory of Hygiene, New Haven, Conn., in partial fulfillment of Army Air Force Contract W-535AC-25002. It was concluded that the most important single factor with which the comfort and efficiency of the pilot are related is the resultant skin temperature of the various areas of the body. Tables, drawings, and charts.

Text. Research J. June 1946

Estimation of the thermal insulation of clothing by measuring increases in the girth of the wearer. (Army Air Forces, Engineering Division, TSEAL-5H-5-241.) Benjamin Libet. O.P.B. Report

PB 5108, 1945; 21 pp.; microfilm, 50¢—photostat, $2.00 (through *Bib. Sci. and Ind. Reports* **1**, 469 (Mar. 22, 1946)).

The "total thickness" method of estimating thermal insulation by measuring girth increase of the wearer as each layer of clothing is added and measuring the thickness of each fabric layer separately is described in detail. A determination of clo for a standing person can be made in an hour within 5–10% accuracy, and the clo for a sitting person is taken to be 10% less. Tables give the thermal insulation values for flying clothing assemblies, clo value of underclothing items of different fit, figures and calculations for one actual run on Assembly 13, and comparison of clo values by the "total thickness" method with other methods.

Text. Research J. June 1946

Effective insulation of Army Air Forces flying clothing—its effect on the onset of sensible perspiration. (Army Air Forces, Experimental Engineering Section, EXP-M-49-695-3A.) A. P. Gagge. O.P.B. Report PB 6935, 1942; 9 pp.; microfilm, 50¢—photostat, $1.00 (through *Bib. Sci. and Ind. Reports* **1**, 469 (Mar. 22, 1946)).

A report on "the combined effect of environmental temperature and clothing on the onset of sensible perspiration," by the John B. Pierce Laboratory of Hygiene, New Haven, Conn., as final fulfillment of Army Air Force Contract W-535-AC-25002. Conclusions reached were: (1) the effective insulation of a flying clothing assembly can be quickly reduced if sensible perspiration is trapped as droplets or ice in the clothing itself; and (2) clothing assemblies made from materials with high moisture regain retain their insulative properties for the longest period of use under cold conditions.

Text. Research J. June 1946

Thermal Insulation

Air layers: Thermal properties when bounded by surfaces of high and low emissivity. (Quartermaster Corps, Climatic Research Laboratory Report 4589, 4590.) William L. Goddard and Marvin Van Dilla. O.P.B. Report PB 8251, 1945; 14 pp.; microfilm, 50¢—photostat, $1.00 (through *Bib. Sci. and Ind. Reports* **1**, 723 (Apr. 12, 1946)).

By means of a study of air cells it was found possible to design an unfilled, inflatable sleeping-bag pad possessing from 5 to 6 clo units of insulation protection. A bar frame was used for this study to enable the experimenter to build up a series of air layers of various thicknesses, baffling arrangements, and separating fabrics, respectively. The thermal insulating value of the air layers was measured at a mean air-space temperature of about 120°F. It was learned that air layers reach a maximum insulation value when about ½ in. thick. Beyond this thickness, no increase in thermal insulation value occurs. An increase of about 45% in the thermal insulation value of the air space may be obtained by breaking up the space with triangular-shaped baffles. An increase of 80% may be gained by coating the bounding surfaces with a reflecting aluminum paint. Complete coverage of the bounding surfaces with large aluminum particles insures optimum reflecting properties. Photographs, tables, and diagrams are appended.

Text. Research J. June 1946

Sleeping Bag

Bags, sleeping, mountain, experimental, No. 250-255. Thermal insulation and utility. (Quartermaster Corps, Climatic Research Laboratory Report 61-A-B.) John H. Talbott, Marshall Clinton, Jr., and Alexis I. Shelokov. O.P.B. Report PB 8255, 1944; 47 pp.; microfilm, 50¢—photostat, $4.00 (through *Bib. Sci. and Ind. Reports* **1**, 531 (Mar. 29, 1946)).

Tests were conducted to determine the relative protective value of five grades of experimental mountain sleeping bags differing in the amount and composition of filling components to be used in place of the 40–60 mixture of down and feathers used in regular mountain sleeping bags, to determine the effect of one laundering on the thermal insulation of these bags, and to compare insulation and other properties of the bags with those of the recently tested 210 series. 14 enlisted men, wearing 50–50 underwear and one pair of wool ski socks, remained in the bags for 6 hrs. in cold chambers at temperatures of −10°F and 0°F. Skin temperatures were recorded every half hr. Tables present data on each bag and results of tests. Graphs are included.

Text. Research J. June 1946

Sleeping bags and sleeping-bag pads. Measurement of thermal insulation by physical procedures. (Quartermaster Corps, Climatic Research Laboratory Reports 182, 185, 193, and 203.) Marvin Van Dilla. O.P.B. Report PB 8244, 1945; 58 pp.; microfilm, $1.00—photostat, $4.00 (through *Bib. Sci. and Ind. Reports* **1**, 531 (Mar. 29, 1946)).

The specific purposes of this study were: (1) to investigate various substitute fills for the mountain sleeping bag, taking into account the effect of a substitution upon the thermal insulation values of the top (uncompressed) and bottom (compressed) sections of the bag; (2) to determine the thermal insulation value of experimental factors for the wool sleeping bag and to compare them with the present standard fabric as well as with each other; and (3) to develop the best type of sleeping-bag pad from the viewpoint of underprotection against cold and moisture as well as that of ease and convenience of carrying. 10 tables, 24 photographs, diagrams, and charts.

Text. Research J. June 1946

German Research

Hosiery Dyeing

The dyeing of hosiery in Germany. (FIAT Final Report 555.) Thomas R. Smith. O.P.B. Report PB 12184, 1945; 5 pp.; microfilm, 50¢—photostat, $1.00

(through *Bib. Sci. and Ind. Reports* 1, 671 (Apr. 12, 1946)).

Hosiery made of natural silk reinforced with mercerized cotton, or stockings made of artificial silk (rayon) and mercerized cotton, are dyed in Germany mostly on mechanical dyeing apparatus and only rarely in smaller lots by hand-suspending on sticks. Two main types of mechanical dyeing apparatus are being used: apparatus similar to the Smith-Drum rotating drum system, and systems in which the stockings are suspended on sticks by means of threads passed through the heels. The stockings of artificial silk had to be cleaned before the dyeing by means of the usual cleaning agent on the basis of alcohol-sulfonates or fatty-acid condensation products in connection with fat solvents.

Text. Research J. June 1946

Glass Fiber

The fibrous glass textile industry. (FIAT Final Report 461.) J. G. M. Leisenring. O.P.B. Report PB 3880, 1945; 27 pp.; microfilm, 50¢—photostat, $2.00 (through *Bib. Sci. and Ind. Reports* 1, 723 (Apr. 12, 1946)).

This report covers an investigation of the fibrous glass textile industry in Germany at the close of World War II. Contrary to experience in America, uses for fibrous glass in Germany have not been developed beyond the original applications, i.e., wool fibers have been used only for domestic and industrial insulating purposes (houses, buildings, boilers, turbines, steam pipes, locomotives, Diesel engines, etc.), whereas textile fibers have been used for only two purposes—electrical insulation and an asbestos substitute. Of the various basic processes described, the Owens and Schüller processes seem the most economically and technically sound. It is questioned whether the Gossler and Hager processes have any long-range value to the German economy, and it seems rather evident that they have no value whatever to the United States. No interesting technical developments in machinery or processes in connection with production of basic fiber have been observed. The carding and spinning of the Schüller fiber by Hardt-Pocorny Company is interesting technically though of doubtful value economically to the American industry. Other fabricating processes observed, such as weaving, were less than ordinary, based on American standards of equipment, output, and product quality. Names, locations, and historical data on plants visited are given in the appendix.

Text. Research J. June 1946

Research on Fibers

Scientific research on cellulose and fibers. Kyle Ward, Jr. O.P.B. Report PB 6354, 1945; 12 pp.; microfilm, 50¢—photostat, $1.00 (through *Bib. Sci. and Ind. Reports* 1, 581 (Mar. 29, 1946)).

Report of visits to following persons: in Germany, Messrs. Elöds, Freudenberg, Jayme, Staudinger, and Weltzien; in Austria, Messrs. Ecker, Kleinert, and Kratky; in Italy, Messrs. Centola and Risso. The object of the interviews with these men was to determine what had been done in the research laboratories in the war years. The report concludes that the research carried on by major investigators has, in general, followed the lines these men had already established for themselves; however, much of it has not been published and publication in full detail would be distinctly to the advantage of American science and industry. Bibliography, pp. 6–11. Complete list of the 570 publications from Prof. Staudinger's laboratory was obtained, but is not included here.

Text. Research J. June 1946

Test Instruments

O. Mecheels, Hohenstein Schloss bei Bonnigheim. (BIOS Final Report 91.) P. Larose and A. C. Burton. O.P.B. Report PB 7913, 1945; 5 pp.; microfilm, 50¢—photostat, $1.00 (through *Bib. Sci. and Ind. Reports* 1, 580 (Mar. 29, 1946)).

Prof. Mecheels directed the Deutsches Forschungs-institut für Textilindustrie at München Gladbach-Rheydt, and is well known for articles on textile developments. The "exact" and "approximate" methods used by Prof. Mecheels for measuring the thermal insulation of fabrics are discussed. A modification of the abrasion tester for fabrics was a mechanism for raising and lowering periodically the abrading surface which was shaped like a half-cylinder of wood, covered with fine emery paper. Prof. Mecheels also worked on testing fibers made with fish protein. He believed that the possibilities of fish protein for fiber purposes were great because it contains an appreciable amount of sulfur and the presence of this sulfur would give the fiber strength.

Text. Research J. June 1946

Textile Education

Textile research and education at Textilingenieurschule Krefeld. Julian F. Smith. O.P.B. Report PB 6346, 1945; 3 pp.; microfilm, 50¢—photostat, $1.00 (through *Bib. Sci. and Ind. Reports* 1, 580 (Mar. 29, 1946)).

The Textilingenieurschule was composed of the Färbereischule, the Webereischule, a school for artificial fiber, a school of textile art, a department of paint and varnish technology, and a department of management. One of the chief contributions of the Textilingenieurschule was conversion of acetate rayon to wool-like fibers.

Text. Research J. June 1946

MISCELLANEOUS

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Cotton Production

Looking ahead with cotton. Prepared by the Bureau of Agricultural Economics and the Extension Service. Miscellaneous Publication No. 584, U. S. Dept. of Agriculture. Washington, Dec. 1945. 22 pp.

Acreage planted to cotton in the United States has declined steadily since the middle 1920's but yield per acre has continued to rise and production has stayed around the

12-million bale mark. This has been due to improved methods for reducing insect and disease damage, better varieties, use of more fertilizer, and better cultural practices. At the same time there has been a trend toward using only those acres and areas which are best adapted to cotton. By use of mechanical methods, cotton can be produced with 25 to 30 hrs. of labor per acre as compared with about 140 hrs. with one-mule equipment and hand picking. Tractors are rapidly displacing mules and there is a trend toward larger farms. In 1925, cotton and cottonseed supplied half the gross income of the 10 principal cotton states, but by 1943 they supplied only $\frac{1}{4}$ of a much larger income, much of which came from other crops and livestock. Only 35% of southern workers were employed in agriculture in 1940 as compared with 60% in 1910. American cotton can no longer take its markets for granted, with the large increases in production of foreign growths, rayon, and competitive paper products. Volume and costs as well as price are determinants of farm income, and the price can be at parity level or higher and still not yield enough for underemployed farm families. Adequate and stable incomes are the real goal of cotton farmers and this goal calls for more efficient utilization of manpower. almost any type of policy can be made to work for a time but the question must be asked, "Where will it put us 10 or 15 yrs. from now?" R. B. Evans

Text. Research J. June 1946

Jute Economics

Jute: Vitally essential product in world trade. Mary E. Poole. *Foreign Commerce Weekly* **22**, 6–11, 44 (Jan. 26, 1946).

Nearly all of the world's jute is grown in Bengal and adjoining provinces in northeast India, where there is a combination of rich, alluvial soil, warm, humid atmosphere, and an abundant supply of cheap labor. The jute crop accounts for $\frac{1}{2}$ of Bengal's cash farm income and jute represents by value 25% of India's total merchandise exports. The history of jute and growing and marketing methods are summarized. About 57% of the world's jute loomage is in India, nearly all of which is on sackings and hessians, including burlap. The industry includes 115 mills with an estimated value of $60,000,000, nearly all located near Calcutta, of which only 30 are administered by Indian interests. Because it makes the cheapest fabric of a given strength that is manufactured, about 70% of the world's jute is used for packaging. It also is used in linoleum, rugs, cordage, roofing felts, tailor paddings, and decoration fabrics. Jute products developed during World War II include "bithess," a prefabricated, bitumized jute carpet used for airplane runways and roads; a cotton-warp and jute-weft canvas used for water-holding stores, water bags, and water storage troughs for the Indian Army; a jute fabric and shellac laminate, "jutlac," used in the construction of military vehicles, in "parajutes" for dropping heavy supplies, and in jettison gasoline tanks. In 1937, the Indian Jute Mills Association established a special research department with laboratories in Calcutta and a branch in London. This department became the Indian Jute Mills Research Institute in 1943. At present the Indian Jute Mills Association is planning a world-wide campaign for the promotion of new and extended uses for manufactured jute, based on data from the Institute, to be initiated in the America's, Australia, and South Africa. The article presents statistical tables on production and exports of raw jute, the size of the Indian jute industry, and exports of jute manufactures from India. R. B. Evans

Text. Research J. June 1946

Jute Fabrics Glossary

A glossary of jute fabrics. *Fibres, Fabrics, and Cordage* **12**, 493–5 (Dec. 1945).

Jute fabrics are named and described. R. B. Evans

Text. Research J. June 1946

Advances in Plastic Technology

Advances in plastics in the United States and Germany. W. C. Goggin. *Chem. and Eng. News* **24**, 339–43 (Feb. 10, 1946).

Comparisons of the production, uses, processes of manufacture and fabrication, and new developments in the United States and Germany are given for vinyl chloride and its copolymers, polystyrene, polyacrylates, cellulose derivatives, polyamides, phenolic resins, urea resins, vinylidene chloride and its copolymers, chlorinated polyvinyl chloride, isocyanates, silicones, polyvinyl carbazole, allyl resins, and plastic foams. E. F. Evans

Text. Research J. June 1946

German Rayon Developments

Technical progress in the German rayon industry. Anon. *Silk and Rayon* **20**, 159, 160, 166 (Feb. 1946).

Extracts from reports published by H. M. Stationery Office on technical progress in the German rayon industry are given. The subjects covered are: (1) the production and use of the cuprammonium rayon production of the Dormagen plant of I. G. Farben; (2) purification of α-cellulose by the hot and cold processes; (3) recovery of basic copper sulfate in producing a cuprammonium fiber; (4) recovery by the wofatite (ion-exchange resin of the bakelite type having active SO_3H groups) filter-recovery process of up to 93% of the copper; (5) crinkled cuprammonium fiber; (6) synthetic upholstering material; (7) continuous spinning of cuprammonium yarn; (8) improved method of esterification of cellulose employing methylene chloride as the solvent; (9) recovery of acetic acid; (10) production of acetic anhydride; (11) acetylation of cuprammonium rayon; and (12) production of polyurethane fibers.* A. L. Merrifield

Text. Research J. June 1946

* The information to which the above abstract refers will be found complete in "Synthetic Fiber Developments in Germany" published by Textile Research Institute.—EDITOR